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TABLE OF CONTENTS

		page	Russ page
75.	Application of the Sechenov Formula to the Solubility of Strong Electrolytes. <u>Zdanovsky</u>	525	577
76.	Thermochemical Investigation of Solutions. IV. Research into the Vapor Pressure and The Constitution of the Vapor of the Binary System $C_2E_5CC_2H_5 + C_2H_5Cl$. <u>Neiman and Demikhovskaya</u>	541	598
77.	Double Decomposition in the Absence of a Solvent. Complex-Compound Formation, Solid Solutions, and Double Decomposition in Melts of Strontium and Barium Fluorides and Chlorides. <u>Bergman and Bukhalova</u>	553	603
78.	Spectrophotometric Investigations of Cobalt-Chloride and Cobalt-Bromide Complexes in Acetone. <u>Barvinok</u>	563	612
79.	Thermochemistry of Complex Cobalt Salts with Neutral Additives. <u>Yatsimirsky and Pankova</u>	569	617
80.	Thermochemical Relationships in the Werner-Miolati Series for Complex Compounds of Cobalt (III). <u>Yatsimirsky and Pankova</u>	577	623
81.	Researches in Formic Acid Systems. <u>Udovenko and R.P. Airapetova</u>	585	632
82.	The Influence of Arginine upon Methanol Solutions of NaI-KI. <u>Sarkisov, Sakharova, Antropov</u>	591	636
83.	Separation of Racemic Glycols of the Acetylene Series into Optically Active Isomers. <u>Zalkind and Efros</u>	599	642
84.	The Structure of Nitrosyl Chloride and Its Condensation Reactions with the Olefins. <u>Yakubovich and Lemke</u>	607	649
85.	Investigation of the Process for the Production of the Methyl and Ethyl Esters of Orthosilicic Acid. <u>Kreshkov and Nessonov</u>	621	660
86.	Research in the Catalytic Conversion of Alcohols into Hydrocarbons of the Divinyl Series. XIV. Catalytic Transformation of Tertiary Butyl Alcohol and Its Binary Mixtures with Methyl Alcohol and Formaldehyde. <u>Gorin and Sonn</u>	625	664
87.	The Reaction of Ethylenediamine with Organic Acids. <u>Dionisyev</u>	631	669
88.	Condensation of Acyl Anilides with Chloral. <u>Berlin, Shchukina, and Sazonova</u>	639	677
89.	Research in Compounds of High Molecular Weight. <u>Korshak, Isbedev, Tsiperstein</u>	647	683
90.	The Mechanism of the Friedel-Crafts Reaction. IX. The reaction of Trichloroethylene with Benzene. <u>Korshak, Smirnovskaya and Andreyeva</u>	655	690
91.	Isomerization in Organomagnesium Synthesis. II. <u>Dubinin</u>	663	696
92.	Steric Hindrances in Organomagnesium Reactions. VIII. The Synthesis of α -Oxyketones. <u>Lapkin and Golokova</u>	669	701
93.	Steric Hindrances in Organomagnesium Reactions. IX. Synthesis of Ketones by the Reaction of Acid Halides with Organomagnesium Compounds. <u>Lapkin and Lyurimova</u>	677	707
94.	Condensation of Benzyl Alcohol with Diatomic Phenols. <u>Zalkind and Gakhniashvili</u>	689	717
95.	Contact Conversion of Furanidine, Pyrrolidine and Thiophane. XXII. <u>Yuryev and Bugorkova</u>	693	720
96.	Conversion of α - and β -Alkyl Furanidines into the Corresponding Thiophanes. XXIII. <u>Yuryev and Gragerov</u>	697	724
97.	Reaction of Diethyl Mercury with Phenols. V. <u>Koton</u>	703	730
98.	Reaction of Diethyl Mercury with Phenols. VI. <u>Koton</u>	709	734
99.	The Photochemical Reaction of Organometallic Compounds of Mercury in Solutions. I. The Reactions of Diphenylmercury. <u>Razumov and Oldekop</u>	711	736
100.	Research in the Anthraquinone Series. XIV. The α, α' -Disulfinic Acids of Anthraquinone. <u>Kozlov and Smolin</u>	717	740
101.	Research in the Anthraquinone Series. XV. The Asymmetrical 1,5-Mercury Compounds of Anthraquinone. <u>Kozlov and Smolin</u>	723	745
102.	Oxidation of Some Sulfides of the Benzothiazole Series. <u>Kucherov</u>	731	752

(Table of Contents is continued on inside back cover.)

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APPLICATION OF THE SECHENOV FORMULA TO THE SOLUBILITY OF STRONG ELECTROLYTES

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If it is assumed that the relative decrease in the solubility of one substance in proportion to the absolute increase in the percentage of another substance in the solution is:

$$-\frac{dx}{x} = cdy,$$

Integration of this initial equation yields:

$$\ln x = \ln x_0 - \text{or } x = x_0 \cdot e^{-cy}.$$

This formula was first proposed by the noted Russian physiologist I. M. Sechenov [1] in 1889 for the solubility of gases in electrolyte solutions of varying composition. In the formula, x_0 and x are coefficients of adsorption of the gas in water and in the solution at $t^\circ = \text{const.}$, y = volumetric concentration of the electrolyte, and c is a constant. The author himself noted that the coefficients of adsorption of various gases did not fully conform to his formula.

In 1891 Sechenov employed a formula analogous to that cited above to compute solubilities in the systems $\text{NaCl} - \text{NaNO}_3 - \text{H}_2\text{O}$ and $\text{KCl} - \text{KNO}_3 - \text{H}_2\text{O}$. When his calculations are compared with Bodlander's experimental data, satisfactory agreement of the two is observed only for a restricted range of volumetric concentrations.

In their investigation of the solubility of acids in solutions of HCl and CH_3COOH , Rendall and Andrews [2] obtained a different kind of curves — with minima and maxima — expressing the constitution of solutions in terms of normality, that did not agree at all with the Sechenov formula cited above. Working with the solubility of H_2S in solutions of HCl , Kapustinsky and Anvayev [3] demonstrated that when the compositions are expressed in moles per liter of solution, a minimum is actually observed to exist, whereas the solubility of H_2S follows Sechenov's law when expressed in moles per kg of water.

In 1927 Rendall and Failey [4] interpreted Sechenov's equation in terms of the activity theory:

$$\ln \gamma = \ln \frac{x_0}{x} = k \cdot \frac{1}{2} \cdot \sum nv^2 = k \cdot y,$$

where γ = coefficient of activity of the dissolved gas, and μ = dissociative power of the electrolyte. They established the approximate constancy of the salting out constants for various gases and nonelectrolytes when acted upon by the same electrolytes.

Morrison obtained good agreement with experiment for the solubilities of nonelectrolytes in salt solutions by introducing a new constant β (usually $\beta < 1$) in Sechenov's formula:

$$\lg x = \lg x_0 - ky^\beta$$

When compositions are expressed in moles per 1000 g of H_2O , k and β are constant over wide ranges of concentration. They depend solely on the nature of the substances chosen and on the temperature.

For very small changes in solubility the Sechenov formula can be transformed into the following form, as Rothmund points out [6]:

$$\frac{x_0 - x}{x_0} = ky \text{ or } x = x_0 - (kx_0)y.$$

This has been confirmed for some systems by the work of Euler [7] and Rothmund [6].

Holluta and Mautner [8] introduced auxiliary terms into the Rothmund-Euler and Sechenov equations for the computation of electrolyte solubilities:

$$\frac{1}{y} \cdot \frac{x_0 - x}{x_0} = k_1 + k_2y \text{ or } \frac{x_0 - x}{x_0} = k_1y + k_2y^2$$

$$\frac{1}{y} \cdot \ln \frac{x_0}{x} = k_1 + k_2y \text{ or } \ln \frac{x_0}{x} = k_1y + k_2y^2.$$

By this means they achieved better, but far from perfect, agreement with experiment (as in the $NaCl - MgCl_2 - H_2O$ and $NaCl - HCl - H_2O$).

With the aid of not very rigid thermodynamic relationships, Jahn [9] derived an equation for the solubilities of slightly soluble nonelectrolytes in fairly dilute solutions of binary electrolytes:

$$\lg x = \lg x_0 + [(1 - \alpha) A + \alpha B] \cdot y,$$

where α = degree of dissociation (found from the electrical conductivity); and A and B are empirical constants with positive and negative signs.

This equation was confirmed in the paper by Knopp [10]. It indicates that in the Sechenov formula c is a linear function of the degree of dissociation of the electrolyte.

Jahn obtained a more complicated equation with many unknowns for the solubilities of electrolytes in solutions of nonelectrolytes and electrolytes without common ions.

The most successful solution of the problem of the joint solubilities of electrolytes has been provided by Akerlof and his associates [11,14], employing activity theory.

The method for calculating solubilities proposed by them is based upon two empirical rules, viz.:

1. The linear variation with concentration of the logarithms of the ratios of activity coefficients of two strong electrolytes of the same valency type in pure solutions:

$$\lg \frac{\gamma_s}{\gamma_R} = k_1 \cdot m \quad \text{or} \quad \lg \gamma_s = \lg \gamma_R + k_1 \cdot \mu_T$$

and 2. A modernized Sechenov formula:

$$\lg \gamma_{\mu_T, s} = \lg \gamma_{\mu_T, R} + k_2(\mu_T - \mu_x) = \lg \gamma_{\mu_T, R} + k_1 \mu_T + k_2(\mu_T - \mu_x),$$

where γ_s and γ_R are coefficients of the activity of two salts taken separately, of the same valency type, for identical values of the concentration m , (in moles per 1000 g of H_2O); the subscript R refers to an electrolyte whose activity coefficients are well known throughout a wide interval of concentrations (HCl); μ_T is the aggregate ionizing power; μ_x is the partial ionizing power of the electrolyte constituting the solid phase; and k_1 and k_2 are constants characterizing the slope of the curve of logarithms of activity coefficients, the former with respect to molarity or aggregate ionizing power, and the second with respect to the partial power of an ingredient with constant aggregate ionizing power.

The value of k_1 remained constant over wide intervals of concentrations in each individual case for 25 mono-monovalent electrolytes examined. Thus they were able to relate the coefficients of activity of such electrolytes as Na_2SO_4 , $MgSO_4$, $CaCl_2$, $Ba(NO_3)_2$, and $K_3Fe(CN)_6$ to the coefficients of activity of HCl for the range of high values of ionizing power ($\mu_T > 10$ as a rule) in the form of the equation:

$$\lg \gamma_s = \lg \gamma_R + k_1 \mu_T + k_1' .$$

The constant k_2 is found from the experimental data for mutual solubility. In some systems (such as NaCl in solutions of $NaNO_3$) it breaks down into two constants:

$$k_2 = k_2' + k_2''(\mu_T - \mu_x) .$$

A link was found between k_2 and k_1 for the simplest mono-monovalent electrolytes. No such relationship could be set up for more complex electrolytes.

On the basis of the constancy of the activity of electrolytes constituting a definite solid phase in various solutions, admitting complete dissociation of the electrolytes in solutions of any concentration, and allowing for the functions cited above, Akerlof develops the following general equation for the solubilities of strong electrolytes:

$$\lg \gamma_{\mu_{T,R}} + k_1 \mu_T + k_2 (\mu_T - \mu_x) + \frac{v_1}{v_1 + v_2} \lg \left[\frac{\mu_R}{v_2 \frac{n_1}{n_1}} + v_3 \frac{\mu_T - \mu_x}{n_2} \right] + \\ + \frac{v_2}{v_1 + v_2} \lg v_2 \frac{\mu_x}{n_1} = \lg \gamma_{s,R} + k_1 \cdot m_s + \lg m_s (v_1 \cdot v_2)^{\frac{1}{v_1 + v_2}}$$

where v_1 and v_3 represent the number of identical ions in the first and second electrolytes; v_2 is the number of ions of opposite sign of the first electrolyte constituting the solid phase; n_1 and n_2 are factors of ionizing power; μ_T and μ_x are the aggregate and partial ionizing power; and m_s and γ_s are the molarity and the coefficient of activity of the saturated solution of the first electrolyte in pure water. For example, the solubility of $MgSO_4 \cdot 7H_2O$ in solutions of $MgCl_2$ at 25° is expressed as follows:

$$\lg \gamma_{\mu_T} HCl - 0.123 \mu_T + 0.0277 (\mu_T - \mu_x) + \frac{1}{2} \lg \frac{\mu_x}{4} + \\ + \frac{1}{2} \lg \frac{4\mu_T - \mu_x}{12} = 0.240,$$

where μ_x is the ionizing power of $MgSO_4$.

For solutions of salts with different ions the foregoing equation is simplified considerably:

$$\lg \gamma_{\mu_{T,R}} + k_1 \mu_T + k_2 (\mu_T - \mu_x) + \lg \frac{\mu_x}{n_1} = \lg \gamma_{s,R} + k_1 \cdot m_s + \lg m_s.$$

The constants of the equations cited remain valid as long as the composition of the solid phase remains unchanged.

The sought-for solubilities for given values of μ_T are found from the equations by successive approximations or by graphic interpolations. As a rule, the differences between the computed and experimental data for strong electrolytes lie within the limits of possible experimental and computational error.

The Akerlof method entails special difficulty in the derivation of solubility equations for double salts and the computation of activities for hydrated forms. In the latter case the simplified equations employed for the activity of water in the form of the linear variation of $\lg a_{H_2O}$ with the concentration of the adulterant are quite suspect. This is evidently why the Akerlof equation for the solubility of Glauber salt in solutions of NaCl do not agree with the experimental data for concentrations of more than 8-10% of NaCl in the mixture.

The equations proposed presuppose the complete dissociation of the electrolytes. They are either not applicable at all to weak and partially dissociated strong electrolytes (such as H_2SO_4 and HNO_3) or they yield a correspondence that is purely fortuitous.

Computations involving the Sechenov formula were made only at 25° , as the requisite, sufficiently reliable data (coefficients of the activity of salts) were

not available for other temperatures. Robinson and Frank [15], on the basis of their data on heat of dilution, assert that the Akerlof rule

$$\lg \frac{c}{R} = k_1 m$$

does not hold for all temperatures.

Thus, the Sechenov formula, suggested at the end of the nineteenth century, has attracted the attention of many researchers over a long period of time. In studying solubilities in various ternary systems it was found that c in the Sechenov formula is not a constant, especially in solutions of two electrolytes. Yet no analysis was made of the inconstancy of c . As a rule, the Sechenov formula was corrected by the formal introduction of new constants.

In the present study, undertaken with a view to determining the mutual solubilities of electrolytes in ternary systems at various temperatures, it was found that the quantity c varies linearly as a function of a , the activity of the water of solution of both electrolytes. This relationship is illustrated in Fig. 1, where $c = \frac{\lg x_0 - \lg x}{y}$ is computed in terms of per cent by weight. The large individual deviations of c from the straight-line relationship for extreme values of a are to be attributed to the high sensitivity of c to absolute errors, even though small, in the values of x and y for small values of the latter. Hence, the solubility of one substance in the presence of another is governed not only by the concentration of the latter but also by the activity of the solvent.

The nature of the variation of c with a , the activity of the solution water, depends upon the way in which the concentrations are expressed.

To facilitate comparison of the values of c obtained for various expressions of concentration, these values for the most characteristic systems were reduced to an identical expression for a single common point by multiplying these quantities by constant factors α with the values indicated in Table 1.

TABLE 1

System	a with concentrations expressed as			
	percent by weight	molec- ular %	gram equiva- lents per liter	gram equiva- lents per 1000 moles of of H ₂ O
NaCl in a solution of MgCl ₂	1	0.2344	0.2526	4.908
NaCl in a solution of HCl	1	0.5319	0.2944	5.888
NaCl in a solution of NaOH	1	0.5480	-	6.764
KCl in a solution of MgCl ₂	1	0.2273	0.2534	4.828
KCl·MgCl ₂ ·6H ₂ O in a solution of MgCl ₂	1	0.2361	0.2623	5.094
Na ₂ SO ₄ ·10H ₂ O in a solution of NaCl ..	1	0.4186	-	4.700

In Fig. 2 there are shown the "reduced" values of c for 25° for concentrations expressed in four basic ways as a function of a , the activity of the water of solution. As is shown in the figure, the best results are obtained when percentages by weight are used; they are somewhat worse when volumetric concentrations (gram equivalents per liter) or molecular percentages are used. Least satisfactory results are obtained with gram equivalents per 1000 moles of water.

In view of the interphase - surface - nature of solution processes it might be supposed that volume concentrations would be the most correct for computing solubilities. The experimental data on solubility in the literature, however, rarely indicate the specific gravity of the solutions. Therefore the most customary percentages by weight were used, especially as they satisfy the linear variation of c with a most satisfactorily.

It follows from Fig. 1 that

$$c = n + ma \quad \text{or} \quad c = k(A - a) ,$$

where n and m, k and A are constants, at constant temperature, that characterize the electrolytes in magnitude and sign, depending on the nature of the salts and adulterants. These equations characterize the overall effect upon the relative magnitudes of the solubility of salts of various factors, such as the method of expressing compositions; the salting-out action of adulterants; electrolytes; the heat of solution of salts; the degree of stability of crystal hydrates; and, in the same instances, the chemical interaction of dissolved electrolytes.

Fig. 2 gives some idea of the effect of the method used to express compositions upon the slope of the line c as a function of a, and hence upon the magnitude of k and A.

An increase in the concentration of electrolytes possessing an ion in common with the salts and differing tendencies to hydration makes itself felt in lowering the solubility of the salts. This salting-out effect of electrolytes is usually accompanied by the simultaneous lowering of the activity of the water of the terminal solutions.

Changes in the heats of solution of salts, bound up with the presence of other electrolytes in the solutions and a reduction in the activity of the water, result in a change in solubilities. The heat of solution increases as the solubility decreases, and vice versa.

An increase in the concentration of the electrolytes is usually accompanied by a decrease in the activity of the water of the solutions; as a result, the stability of the crystal hydrates decreases, while their solubility rises.

The chemical interaction of electrolytes, resulting in a decrease in the number of free molecules and ions of the salt in solution, facilitates the further passage of the salt into solution from the solid phase. In these cases of systems with chemical affinities that are in general interpreted by our formula, the constants k and A, which in other electrolytes that do not react chemically with the salt are functionally interrelated, usually possess specific values.

Thus the solubilities of most salts are covered by the general formula:

$$\lg x = \lg x_0 \pm k(A - a) y ,$$

in sufficiently satisfactory agreement with experimental data, where k and A are constants characterizing the change in the solubility of salts in the presence of electrolytes.

With t° = constant, k remains constant throughout the solubility curve for the given salt in the presence of another electrolyte. The variation of k with t° is usually linear throughout the range 0-100°. The value of k varies for various admixtures - electrolytes. Thus, this constant characterizes the salting-out

Table 2
Values of the constants k and A in solubility formulas for various dissolved salts and electrolyte admixtures

No.	Dissolved salt	Electrolyte admixture	Temperature range	$\lg z = \lg z_0 - k(A-a-y)$		Remarks
				a	A	
1	NaCl	KCl	0-100°	0.0375-0.000085		
2		NH ₄ Cl	0-100	0.0425-0.000135		
3		MgCl ₂	0-105	0.0225-0.00021		
4		CaCl ₂	25-115	0.0820-0.0030		
5		HCl	0-30	0.1117-0.0019		No. 1 at $y < 35\%$
6		Na ₂ SO ₄	0-100	0.0383-0.0007		
7	Na ₂ CO ₃	Na ₂ CO ₃	0-60	0.08		
8		NaNO ₃	0-100	0.0297-0.00048		
9		NaCl	0-100	0.0303-0.0006		
10	KCl	NH ₄ Cl	0-100	0.0303-0.0006		
11		MgCl ₂	0-100	0.0368-0.001	2.4-0.03	Not accurate for No. 10
12		CaCl ₂	0-50	0.0335-0.00092		No. 12 at $y < 30\%$
13		HCl	0-50	curvilinear		No. 13 at $y < 25\%$
14	KCl · MgCl ₂ · 6H ₂ O	MgCl ₂	0-100	0.1397-0.000575	0.95-0.02	
15	Na ₂ SO ₄ · 10H ₂ O	NaCl	0-30	-0.1390+0.0029	0.57-0.004	
16		NaCl	0-30	-0.135+0.0031		
17		Na ₂ CO ₃	0-30	-0.0703+0.00155	0.6	
18		MgSO ₄	0-30	-0.001-0.00078		
19	Na ₂ SO ₄	NaCl	20-95	0.0780+0.000116	1.25-0.01	
20	MgSO ₄ · 7H ₂ O	MgCl ₂	0-55	$k \rightarrow 0$	$kA = 0.0375-0.00034$	
21		K ₂ SO ₄	0-30	$k \rightarrow 0$	$kA = 0.000221$	
22	Na ₂ SO ₄ · MgSO ₄ · 4H ₂ O	Na ₂ SO ₄	25-75	0.078	1	
23		MgSO ₄	25-75	0.110		
24	Na ₂ CO ₃ · 10H ₂ O	NaCl	0-30	-0.0767+0.000131	0.57-0.005	
25		Na ₂ SO ₄	0-30	-0.0338		

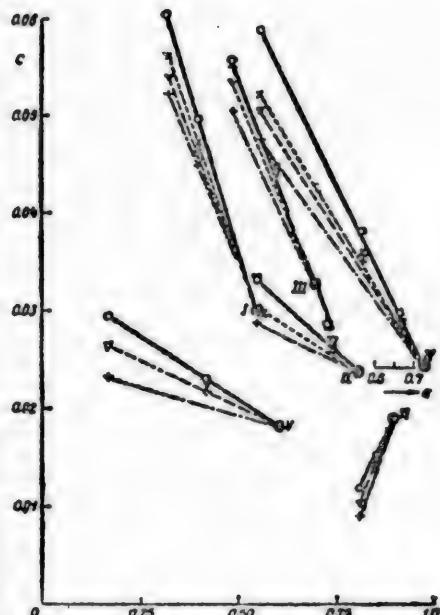


Fig. 2 Reduced values of c for various expressions of composition as a function of a , the activity of the water of solutions at 25°.
Legend: 0 - in percent by weight; x - in grams per liter; φ - in mol. percent; --- in gram equivalents per 1000 moles of water.
•: common reduction point.
I - NaCl · MgCl₂ · 6H₂O in solutions of MgCl₂; II - KCl in solutions of MgCl₂; III - NaCl in solutions of HCl; IV - NaCl in solutions of NaOH; and VI - Na₂SO₄ · 10H₂O in solutions of NaCl.

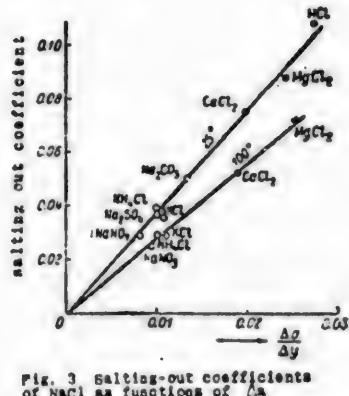


Fig. 3 Salting-out coefficients of NaCl as functions of a/y

at 25° and 100°
At 25°, $\Delta a = 0.75 - 0.65$; at 100°, $\Delta a = 0.72 - 0.62$; Δy - difference in the concentration of electrolytes in pure solutions at the given values of a and y . The point O lies in the region of extrapolated values of a .

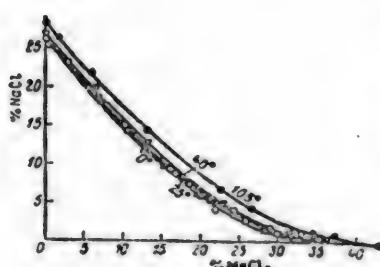


Fig. 5 Solubility of NaCl in MgCl₂ Solutions

Legend: X - 0°, Kurnakov and Zhuchzhny /24/; O - 25°, Kurnakov and Zhuchzhny /24/, STE /20, p. 57/; □ - 25°, ▽ - 40°, ▲ - 100°, GIPKh /23, p. 58/; + - 50°, STE /20, p. 52/ and Keitel /21, p. 1281/.

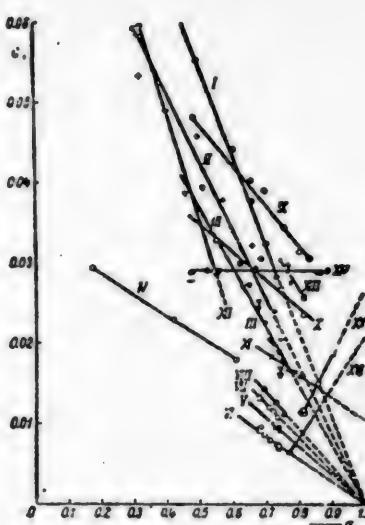


Fig. 1 Variation of c in the formula $\lg z = \lg z_0 - ky$ with a , the activity of the water of solution, at 25°. (composition expressed in w/w %).

Legend: I - NaCl in a solution of HCl; II (+) - NaCl in a solution of MgCl₂; III -- NaCl in a solution of CaCl₂; IV - NaCl in a solution of NaOH; V - NaCl in a solution of Na₂SO₄; VI - NaNO₃ in a solution of NaCl; VII - NaNO₃ in a solution of NaCl; VIII - NaCl in a solution of NaCl; IX - NaCl in a solution of HCl; X - KCl in a solution of MgCl₂; XI - KCl in a solution of NaCl; XII - NaCl · MgCl₂ · 7H₂O in a solution of NaCl; XIII - Na₂SO₄ in a solution of NaCl; XIV - MgSO₄ · 7H₂O in a solution of NaCl; XV - Na₂SO₄ · 10H₂O in a solution of NaCl; XVI - Na₂CO₃ · 10H₂O in a solution of NaCl.

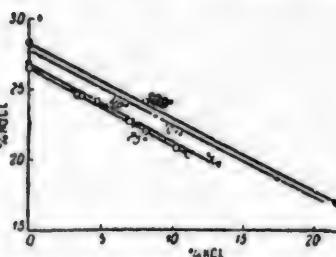


Fig. 4 Solubility of NaCl in Solutions of KCl

Legend: O - 25°, ▽ - 100°, STE /20, p. 57/; □ - 25°, ▽ - 40°, ▲ - 100°, GIPKh /23, p. 58/; + - 50°, STE /20, p. 52/ and Mukerje /21, p. 521/.

effect of various electrolytes. It depends on the ability of the electrolytes to bind water (to reduce the activity of water) and to form chemical compounds with the salt in solution.

As computations indicate, of the two constants k and A , the latter may be found from the former by means of a simple equation:

$$A = \alpha + \frac{\beta}{K} ;$$

where α represents a , the activity of water in solutions of two electrolytes, while β represents the value of c at the point of intersection of the family of straight lines c/a for various systems with a single constant solid phase (Fig. 1.) and for various temperatures. The constant A is determined, in general, by the nature of the dissolved salt. The values of the constants, as determined for a number of systems, are listed in Table 2.

On the basis of the solubility of NaCl in solutions of other electrolytes at 25° and 100° (for NaCl, $A = 1$) a link was found between various salting-out constants k and the values of the relative lowering of the activity of water corresponding to unit concentration of the second electrolytes $\left(\frac{\Delta a}{\Delta y}\right)$, taken separately, in the vicinity of the water activities that are characteristic of saturated solutions of table salt (Fig. 3). An analogous relationship, but with a different slope of the line $k/\Delta a$, is plotted for KCl. The existence of ratios of this sort enable us to determine the probable values of k for the value $\frac{\Delta a}{\Delta y}$ of individual electrolytes and from this to predict solubility curves for the simplest ternary systems that do not form binary compounds.

The values of a , the activity of water in the solutions of some electrolytes may be computed from the activity of the solution water of the individual electrolytes by means of the author's formula derived earlier and experimentally tested [18,17].

$$\frac{x}{x_0} + \frac{y}{y_0} + \dots = 1,$$

where x, y, \dots are the given concentrations of the electrolytes in a common solution; and x_0, y_0, \dots are the concentrations of the same electrolytes in binary solutions with the same water activities that satisfy the equation.

Let us assume that we are to find the activity of the solution water, a , containing 20.42% NaCl and 11.14% KCl at 25° (a saturated solution of both salts). For this purpose, we find the values of x_0 and y_0 for the sought-for activity of water that satisfy the equation:

$$\frac{20.42}{x_0} + \frac{11.14}{y_0} = 1 .$$

Let us take $a' = 0.73$. Then:

$$\frac{20.42}{27.8} + \frac{11.14}{37.8} = 1.0292.$$

whence $x_0 = 1.0292 \cdot 27.8 = 28.61\%$ NaCl and $y_0 = 1.0292 \cdot 37.8 = 38.72\%$ KCl.

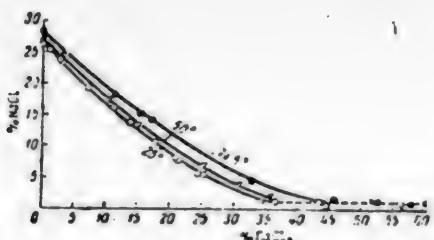


Fig. 6 Solubility of NaCl in CaCl₂ solutions

Legend: 0 - 25°, Cameron, Bell, and Robinson /20, p. 53/; Mile and Wells /21, p. 642/; ▽ - 50°, Pelling and Robertson /20, p. 53/; and /2, p. 1141/; Lukyanov and Shokhet /28/; ◆ - 94.5°, Pelling and Robertson /20, p. 53/; X - 100°, Lukyanov and Shokhet /28/.

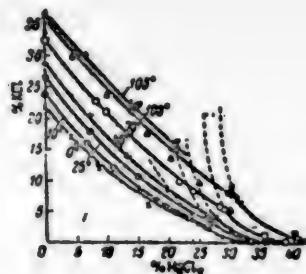
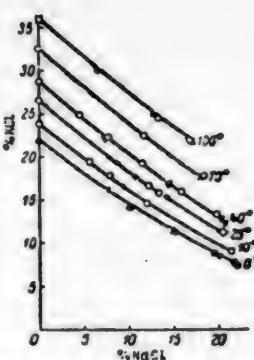


Fig. 8 Solubility of KCl and KCl·MgCl₂·H₂O in the KCl - MgCl₂ - H₂O system.

Legend: X - 0°, Palkin /23, p. 80/; 25°; 0 - 25°; 0 - 70° and ▽ - 100°, GIPKh /23, p. 59/; A - 100°, Campbell, Downes, and Samis /31/; X - 100°, Precht and Midgen /21, p. 517/; ▽ - 105°, Keitel /21, p. 1250/.

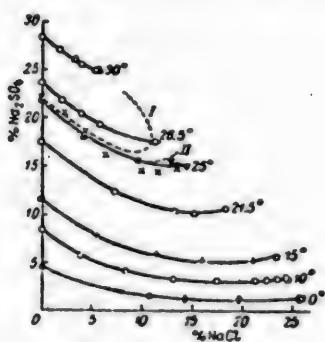


Fig. 9 Solubility of Na₂SO₄·10H₂O in NaCl solutions

Legend: 0 - Seidell /21, p. 669/; ◆ - SIE /20, p. 26/; X - Cameron, Bell and Robinson /20, p. 26/; + - Schrinemakers and Haat /21, p. 669/; ▽ - Kurnakov and Zheshchushny /24/; △ - Schrotter /22, p. 101/; ○ - Takegami /21, p. 1423/; ◇ - Pelling /21, p. 1423/; and □ - Pelysh /30/.

Fig. 7 Solubility of KCl in NaCl Solutions

Legend: 0 - GIPKh /23, p. 57/; ◆ - Palkin /23, p. 70/; + - Reinders /20, p. 57/; X - Konck and Krombach /22, p. 55-69/; ▽ - Lite and Mukerji /22, 67/.

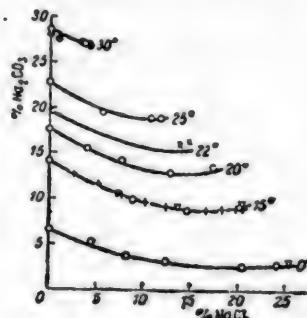


Fig. 10 Solubility of Na₂CO₃·10H₂O in solutions of NaCl.

Legend: 0 - Frith /20, p. 41/; ◆ - Kochert /20, p. 40/; ▽ - M. Monval /21, p. 1413/; + - Reich /21, p. 635/; X - Makarov /20, p. 221/.

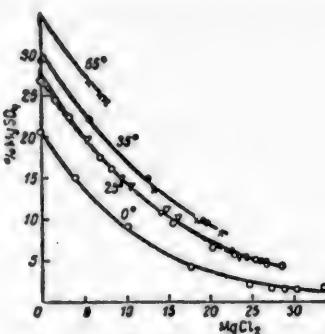


Fig. 11 Solubility of MgSO₄·7H₂O in MgCl₂ solutions.

Legend: 0 - Kurnakov and Zheshchushny /24/; ◆ - Kurnakov and Kuznetsov /25/; 0 - Kuznetsov /26/; X - Voskresenskaya /27/; + - Kurnakov /22, p. 128/; ▽ - Takegami /21, p. 127/.

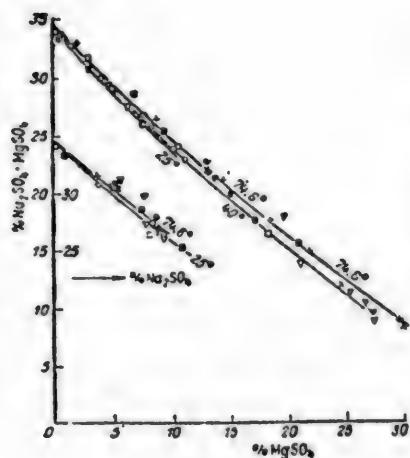


Fig. 12 Solubility of astrakanite in solutions of MgSO₄ and Na₂SO₄.

Legend: 0 - 25°, Kurnakov and Zheshchushny /24/; Archibald and Haley /21, p. 1287/; Banerth /22, p. 134/; Takegami /21, p. 1286/; ◆ - 30°, Archibald and Haley /21, p. 1287/; Rosenboom /22, p. 135/; □ - 35°, Rosenboom /22, p. 135/; + - 40°, Banerth /22, p. 136/; X - 50°, Voskresenskaya /27/; ■ - 40° and X - 50°, Archibald and Haley /21, p. 1287/; △ - 50°, Archibald and Haley /21, p. 1287/; ▲ - 55°, Banerth /22, p. 136-137/; △ - 55°, A'Ami /22, p. 137/; + - 74.5°, Schrinemakers /22, p. 135/; X - 60°, Archibald and Haley /21, p. 1287/.

For the first solution, $\underline{a} = 0.716$; for the second, $\underline{a} = 0.72$.

$$\text{The sought-for } \underline{a}: \frac{3}{4} 0.716 + \frac{1}{4} 0.720 = 0.717.$$

According to van't Hoff's experimental data [18] $a = \frac{16.84}{23.50} = 0.7166$; according to the data of Leopold and Johnston [19] $\underline{a} = \frac{16.98}{23.76} = 0.7146$.

Thus, the computed value of \underline{a} is in good agreement with the values found experimentally, in spite of the fact that according to the present author [17], when isopiestic solutions of NaCl and KCl are mixed together, an exothermic effect of the interaction between the hydrated molecules and ions of the electrolytes is observed.

An equation of the form $\lg x = \lg x_0 + k(A - a) \cdot y$ was successfully employed in calculating the solubilities of NaCl, KCl, carnallite, sodium sulfate, astrakanite, epsomite, and soda in solutions of various electrolytes in the temperature range from 0° to $100-105^\circ$.

In establishing the values of the constants entering into our formula from the data in the literature relating to various ternary systems with a single constant solid phase, we found the value $c = \frac{\lg x_0 \lg x}{y}$ and a , the activity of the water of the corresponding solutions. Then the coordinates a and β of the point of intersection of all the straight lines c/a .

The sought-for quantities k and A were found by simultaneously solving two equations:

$$A = a \pm \frac{\beta}{k} \quad \text{or} \quad \beta = \pm k(A - a) \quad \text{and} \quad c_1 = \pm k(A - a_1),$$

where $c_1 = \frac{\lg x_0 - \lg x_1}{y_1}$ and a_1 is the activity of the water of a solution with the electrolyte concentrations x_1 and y_1 , corresponding to the most reliable point on the experimental solubility curve for $t^\circ = \text{const}$.

As a rule, the constants k thus determined are expressed as linear functions of the temperature (in the range of $0^\circ - 100^\circ$): $\underline{k} = k_1 + k_2 t$.

Let us cite some of the most typical examples to illustrate the applicability of this new equation.

For the solubility of NaCl in solutions of various electrolytes at various temperatures we have $\lg x = \lg x_0 - k(1-a)y$. We take the values of x_0 for NaCl from the Spravochnik Tekhnicheskoi Entsiklopedii (STE "Technical Encyclopedia Handbook") Vol. 5, p. 259.

The data for the system NaCl - KCl - H₂O are shown in Fig. 4. The deviation of the computed solubility values for NaCl from the experimental values does not exceed $\pm 0.15\%$, as a rule. The deviation of -0.39% from the GIPKh data, at $t = 75^\circ$, observed in one instance is not found in such magnitude for a similar solution at $t = 75^\circ$; according to the STE data, $\Delta_{\text{NaCl}} = -0.04\%$. Hence, the Δ_{NaCl} of 0.4% should be ascribed to an accidental experimental error.

The data for the NaCl - MgCl₂ - H₂O system are shown in Fig. 5. When the

percentage of $MgCl_2$ in the solution varies from 0 to 35-37°, the activity of the solution water ranges from 0.75 to 0.32. Over this whole range the computed solubility curves (solid lines) agree satisfactorily with the experimental data.

A special experimental check of the solubility of $NaCl$ in the area of high concentrations of $MgCl_2$ (12.7 - 34.7%) indicated a total discrepancy between the experimental and computed solubility values lying within 0.02% - 0.04% for $NaCl$.

For the system $NaCl - CaCl_2 - H_2O$ the agreement between the calculated and experimental values of $NaCl$ solubility for $CaCl_2$ percentages in the solutions ranging up to 35-45% ($a = 0.45 - 0.40$) is satisfactory (within the limits of experimental error). At higher $CaCl_2$ concentrations, however, the calculated solubility of $NaCl$ approaches zero asymptotically, as shown in Fig. 6, while the experimental value of the solubility remains constant (about 1%).

An experimental check made by the author at 25° indicated a decrease in solubility of $NaCl$ when the percentage of $CaCl_2$ in the solution rose to 51%. At concentrations that are higher than 35-40% it is actually found that the calculated values of $NaCl$ solubility deviate from the experimental values by 0.14-0.25% of $NaCl$. It may be that a discrepancy of this sort is linked either with the existence of a double salt of $NaCl$ and $CaCl_2$ in the solution or with the presence of supplementary solubility of $NaCl$ in the dissolved $CaCl_2$.

The agreement between the literature data and the experimental solubility values is good enough for the solubilities of $NaCl$ in other electrolytes. The discrepancies are attributable to experimental error. A similar result was obtained even for a solution of $NaNO_3$, the concentration of which went as high as 50-58% as the $NaCl$ content dropped to 7.5-5%. The same may be said of the solubility of $NaCl$ in solutions of HCl . It should be noted, however, that in the latter case there is a curvilinear variation of the constant k with temperature, if we are to be guided by the data of Kurnakov and Henke [20, p. 203, 210]. If it is borne in mind that according to these authors the solubility of $NaCl$ at 25° is lower than that given in the other literature sources, it may be supposed that their 80° isotherm is not comparable with those taken for the data calculated by Engel, Akerlof, Masson, and Schrimmakers at temperatures of 0-30°.

The solubility of KCl in solutions of other electrolytes is expressed by the formula $lg x = lg x_0 - k(A - a)y$, where $A = 2.4 - \frac{0.03}{k}$. The solubility of KCl in water (x_0) is taken from the symposium Solikamskie Karnallity ("Solikamsk Carnallites"), p. 57, 1935, and STE, vol. 5, p. 260.

The data for the $KCl - NaCl - H_2O$ system are shown in Fig. 7. They are characterized by good agreement between computation and experiment.

In the $KCl - HCl - H_2O$ system at temperatures from 0° to 50°, as well as in the $NaCl - CaCl_2 - H_2O$ system (according to the literature data) the solubility of KCl is found to remain constant for concentrations of HCl above 30%. The discrepancy between the computed and the experimental solubility figures for solutions with a high percentage of HCl may be explained in this case as due to the formation of a new solid phase $KCl \cdot HCl$ and $KCl \cdot 2HCl$, discovered by Duboux [32] in his study of the solubility and viscosity of the corresponding solutions.

In Fig. 8 there are shown the solubility of KCl and carnallite in the $KCl -$

$\text{-MgCl}_2 - \text{H}_2\text{O}$ system, the dotted lines indicating the hypothetical metastable portions of the solubility curves for carnallite. The agreement between the computed solubility values (solid lines) and those found experimentally is quite satisfactory in most cases. Only at 100° do the data of the German authors lie higher, and those of the American authors lower, than the curve of calculated KCl solubilities. These two-sided deviations are doubtless bound up with experimental errors, especially as the calculated solubility curve agrees very well with the GIPKh data for the same isotherm.

The solubility of Glauber salt in solutions of other salts is of special interest. For this salt, $\lg x = \lg x_0 - k(a - A)y \cdot x_0$ is taken from the STE data, (v.7, p.26) and the Seidell handbook (1919, p 667). For $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ all the c/a straight lines pass through a common point with the coordinates of $c = 0$ and $a = 0.60$. Hence, in this case $A = 0.6$.

The solubility of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in NaCl solutions in the 0-30° range is shown in Fig. 9. The computed (solid) curves of solubility coincide with almost all the experimental data.

That is why the correctness of the data of Cameron, Bell, and Robinson for 25°, which fall outside the general family of the solubility curves, appears to be extremely doubtful.

Figure 9 also shows, for the sake of comparison, the solubility of Glauber salt in NaCl solutions at 25°, computed by the Akerlof formula:

$$\lg \gamma_{\text{HCl}, \mu_T} = 0.188 \mu_T + 0.001 \mu_T - \mu_x + \frac{1}{3} \lg \frac{\mu_x}{3} + \frac{2}{3} \lg \mu_T - \frac{\mu_x}{3} = -0.118,$$

by the successive choice of partial ionizing powers μ_x for the selected aggregate ionizing powers μ . As the dotted line I indicates, the values directly computed by us diverge quite distinctly from the experimental values at the maximum possible NaCl percentage of 11%. According to Akerlof's own calculations, shown by him in a graph and exhibited by us as the dotted curve II, a marked deviation of the computed solubility of Glauber salt from the experimental data is likewise observed for NaCl concentrations above 11%.

The agreement between the experimental solubilities of Glauber salt and those computed by our formula is also found to be satisfactory in the presence of MgSO_4 and Na_2CO_3 . Here too we find some deformation of the lines.

Anhydrous Na_2SO_4 behaves somewhat differently than Glauber salt in NaCl solutions:

$$\lg x = \lg x_0 - k(A - a)y, \text{ where } A = 1.25 - \frac{0.01}{k}.$$

The computed solubility values, particularly at 25, 50, and 95°, agree rather well with the literature data ($\Delta\text{NaCl} = 0.2\text{-}0.4\%$). The biggest discrepancy, occurring in the solutions containing some 25% of NaCl, is accidental in nature.

The solubility of the decahydrate of soda in the presence of NaCl and Na_2SO_4 varies in accordance with the same law as that of Glauber salt. For $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ $\lg x = \lg x_0 - k(a - A) \cdot y$, where $A = 0.5 + \frac{0.005}{k}$. The agreement between computation and experiment is found to be the same as in the Glauber salt systems. By way of illustration we show the solubility of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in solutions of NaCl

in Figure 10.

The solubility of $MgSO_4 \cdot 7H_2O$ in solutions of other electrolytes is expressed by the very simple formula $\lg x = \lg x_0 - ky$. The solubility of epsomite in water is taken from the Seidell handbook (p. 396).

The data for the $MgSO_4 - MgCl_2 - H_2O$ system are given in Fig. 11. The 55° curve represents the metastable solubility of $MgSO_4 \cdot 7H_2O$. The solubility of epsomite, computed by the Akerlof formula, is represented by the dotted line. All the data are in rather good agreement.

The solubilities of $MgSO_4 \cdot 7H_2O$ in solutions of Na_2SO_4 listed in the Seidel and "Technical Encyclopedia" handbooks are extremely contradictory. That is why we have not made use of them. The data in the literature on the solubility of epsomite in K_2SO_4 solutions are very few in number and not reliable enough. The solubilities computed for the latter systems are in sufficiently good agreement with the basic data.

The fairly considerable discrepancies in the mutual solubilities of sodium, potassium, and magnesium sulfates encountered in the literature are due to the phenomena of supersaturation, the slowness with which equilibrium is reached, and errors in method. This also holds for the determinations of the solubilities of astrakanite in solutions of Na_2SO_4 and $MgSO_4$.

Processing of the materials in the literature disclosed that the solubility of astrakanite in water remains practically unchanged as the temperature changes, corresponding to 34.65% of anhydrous astrakanite. This value of x_0 was employed in calculations.

Figure 12 shows the solubility of $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ in solutions of Na_2SO_4 and $MgSO_4$, computed from the formula $\lg x = \lg 34.65 - k(1-a)y$, where $k = 0.078$ for Na_2SO_4 and 0.110 for $MgSO_4$. If we take into account the difficulties of determining the solubility of astrakanite experimentally mentioned above and the experimental errors thereby occasioned (sometimes amounting to as much as 2%), the agreement between computation and experiment must be acknowledged to be good enough.

A method of computing the solubilities of salts in quaternary and more complex systems, based upon the simple principle of the additive change in solubilities when isoactive solutions are mixed together, is described in another paper (Journal of Physical Chemistry USSR, 1948, v. 22, p. 12).

In conclusion the author wishes to express his heartfelt gratitude to L. L. Ezrokha, who assisted in the computations for the present paper.

CONCLUSIONS

1. The solubility of substances in electrolyte solutions is expressed as follows:

$$\lg x = \lg x_0 - cy,$$

in the Sechenov formula, where x_0 and x are solubilities in pure water and in electrolyte solutions of concentration y , and c = a constant.

2. When applied to the solubilities of salts in solutions of other

electrolytes, the quantity c varies linearly as a function of the activity of the water of solution of both electrolytes. This variable can be represented by two constants k and A:

$$c = k(A - a),$$

where a is the activity of the water in the solutions of the two electrolytes, computed by the method of A.B.Zdanovsky.

3. The auxiliary constant A is found from the salting-out coefficient k by a formula that holds good for all systems and temperatures:

$$A = a \pm \frac{\beta}{k},$$

where a represents the water activity a, and β is the value of c at the point of intersection of the straight lines c and a.

4. For some salts (NaCl, KC1) the constants k, which have different values in the presence of different electrolytes, may be determined from the relative lowering of the activity of the water of the separate electrolytes used, and from them, in turn, we can obtain the solubility curves of the salts in the presence of the given electrolytes.

5. The deviation of the experimental values of the solubility from those computed by the formula $\lg x = \lg x_0 - k(A - a)$ do not, as a rule, exceed the limits of experimental error.

6. The new exponential solubility formula makes possible a generalization of the data in the literature, bringing to light the most probable solubility value, and fills in the gaps in the polythermic solubility diagrams for ternary systems.

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THERMOCHEMICAL INVESTIGATION OF SOLUTIONS

IV. RESEARCH INTO THE VAPOR PRESSURE AND THE CONSTITUTION OF THE VAPOR OF THE BINARY SYSTEM $C_2H_5OC_2H_5 + C_2H_5Cl$

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I. INTRODUCTION

As we know, knowledge of the vapor pressure and the composition of the vapors at various temperatures is required for computing the distillation of binary mixtures.

Encountering the necessity of separating diethyl ether from its mixtures with ethyl chloride, we found absolutely no data in the literature on the vapor pressure and the composition of the vapors of this binary system.

After the classic work of Gibbs [1] and the Russian physical chemist Konovalov [2], the investigation of vapor pressure and vapor composition is of considerable theoretical interest, enabling us to draw a conclusion concerning the chemical interaction of the components in the formation of solutions.

In pursuing the above goal, we set up a regular investigation of the vapor pressure and the composition of the vapor of solutions of diethyl ether and ethyl chloride.

II. EXPERIMENTAL METHOD

The diethyl ether used in the research was prepared from anesthetic ether. To eliminate traces of peroxides and aldehydes from the latter, it was treated with an alkaline solution of $KMnO_4$ for 24 hours; the ether was then washed with distilled water, dried with calcium chloride, and redistilled. The fraction boiling at 34.6° at 760 mm was used in our tests. The density of the ether was $d_4^{15} 0.719$, which is in good agreement with the literature data, [3].

The vapor pressure of the ethyl ether purified by us is shown in Table 1 for various temperatures.

As Table 1 indicates, the vapor pressure of our sample of diethyl ether agrees very well with the handbook data [4], which testifies to the purity of the

ether employed in the present research.

TABLE 1
Vapor Pressure of $C_2H_5OC_2H_5$ at Various Temperatures

Tempera-ture	P_{mm} from our data	P_{mm} from handbook	Δmm
0°	187.3	186.0	+ 1.3
2.7	215.0	—	—
4.0	225.0	—	—
5	234.8	233.0	+ 1.8
7	255.0	—	—
10	290.0	291.5	- 1.5
15	360.0	360.5	- 0.5
20	445.0	442.0	+ 3.0
22.2	485.0	—	—
25	539.0	537.0	+ 2.0
28	600.0	—	—
30	649.0	647.0	+ 2.0
33	718.0	—	—
35	775.0	775.5	- 0.5

The ethyl chloride was distilled, and its purity was checked by determining its vapor pressure at various temperatures.

The results of our determinations are listed in Table 2.

TABLE 2
Vapor Pressure of C_2H_5Cl at Various Temperatures

Tempera-ture	P_{mm} from our data	P_{mm} from handbook	Δmm
2.7°	549	—	—
5	569	575	- 6
10	685	692	- 7
15.6	846	835	+ 11
20.2	988	996	- 8
25	1175		
30	1395		
35	1679		

These results agree very well with the handbook data [5], testifying to the adequate purity of the ethyl chloride.

In determining the vapor pressure of mixtures of $C_2H_5OC_2H_5 + C_2H_5Cl$, we made use of the setup shown diagrammatically in Fig. 1.

The mixture under test was enclosed in ampoule 2, connected to manometer 3 and placed in the thermostat 1. The latter is filled with water, which is heated by the nichrome coil 4 and stirred by the stirrer 5. The temperature is maintained constant by the toluene temperature-control device 6 with an accuracy of 0.1°.

To prevent the condensation of the vapors escaping from the thermostat, the tube leading to the manometer is heated by the current flowing through a nichrome coil. The volume of ampoule 2 and of the connecting tubes filled with vapor was small compared to the volume of the solution, and, as calculations indicated, the composition of the liquid did not change appreciably during evaporation. The error in measuring the vapor pressure with the apparatus described usually did not exceed 0.5%.

The mixtures of varying concentration employed for the tests were placed in the vessel 2 shown in Fig. 1, which was connected to a vacuum pump through an outlet tube. Vessel 2 was immersed in a Dewar flask containing liquid air, after which the air was exhausted from vessel 2. Vessel 2 was disconnected from the pump by turning a vacuum stopcock, and the mixture of diethyl ether and ethyl chloride was thawed out. During this, part of the dissolved water passed into the gas phase. The thawing out and the evacuation of the gases was repeated several times until all the air had been eliminated from the system. The vessel was then unsoldered from the vacuum apparatus, replaced in thermostat 1, and the vapor pressure of the mixture was measured several times at different temperatures.

After the series of measurements was complete, vessel 2 was unsoldered from the manometer, and the mixture was subjected to chemical analysis. The branch tube of vessel 2, containing the congealed mixture was sawed off, after which the vessel was placed in an autoclave with 50-100 ml of an anhydrous solution of KOH in alcohol. The autoclave was closed hermetically and the C_2H_5Cl was saponified for 1 hour at 100°. After cooling, the contents of the autoclave were transferred to a glass, the solution diluted with distilled water, acidulated with nitric acid, and transferred to a measuring flask. The chlorine-ion content was determined by titration by the Volhard method. Knowing the weight and the chlorine content of the mixture, we can easily compute its molecular composition.

III. EXPERIMENTAL RESULTS

a) Variation of Vapor Pressure with Temperature

We made tests to determine the vapor pressure at various temperatures of a series of mixtures of $C_2H_5OC_2H_5$ and C_2H_5Cl . The results of the analysis of the solutions employed in these tests are listed in Table 3.

We determined the vapor pressure of each of these solutions at various temperatures in the range of 0-35°C.

The results of our measurements are depicted in Fig. 2 as curves of $P = f(T)$.

As may be seen in Fig. 2, the vapor pressure of these solutions changes

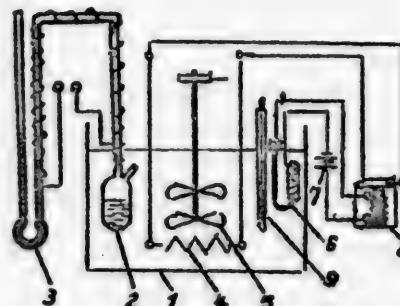


Fig. 1 Diagram of Apparatus

1-thermostat; 2-vessel containing solution; 3-manometer; 4-heating-coil; 5-stirrer; 6-temperature control; 7-storage battery; 8-relay; 9-thermometer.

regularly as their composition changes. This means that there are neither maxima nor minima in the curves of the vapor pressure as a function of solution composition, and, hence, diethyl ether and ethyl chloride do not form azeotropic mixtures in accordance with Konovalov's law [2].

TABLE 3

Composition of Solutions of $C_2H_5OC_2H_5 + C_2H_5Cl$

Ampoule No.	Content (g)		Per cent of ethyl chloride	
	C_2H_5Cl	$C_2H_5OC_2H_5$	By weight	Molecular
1	0.1815	0.8335	17.9	19.6
2	0.562	0.782	41.8	45.3
3	0.609	0.635	49.0	52.1
4	0.998	0.485	67.8	70.0
5	0.856	0.085	90.9	92.0

b) Heat of Vaporization

As the work of Clausius and Clapeyron proved, the variation of the vapor pressure of pure liquids with the temperature is expressed by the differential equation:

$$\frac{d \ln P}{dT} = \frac{\lambda}{RT^2}, \quad (1)$$

where λ is the molecular heat of vaporization.

For small temperature intervals it may be assumed that $\lambda = \text{constant}$. Under this assumption Equation (1) may be integrated, yielding:

$$\lg P = A - \frac{\lambda}{4.57} \cdot \frac{1}{T}. \quad (2)$$

If we plot the data of our experiments with pure diethyl ether and ethyl chloride, using $\lg P$ and $1/T$ as co-ordinates, as in Fig. 3, the experimental data lie along the straight lines 1 and 4. The molecular heat of vaporization of diethyl ether, $\lambda = 6800 \text{ cal/mole}$, and that of ethyl chloride, $\lambda = 5950 \text{ cal/mole}$, may be computed from the slopes of these lines. The quantities found in our experiments are in good agreement with tabular data: 6650 and 5970 cal/mole [6].

The variation of the vapor pressure of the solutions with temperature may also be represented by formula (2), but in this case, as Vrevsky has pointed out [7], λ depends on the heat of solution as well as upon the molecular heat of vapor formation of the components.

The experimental data obtained by us for the vapor pressure of solutions of $C_2H_5OC_2H_5 + C_2H_5Cl$ are also represented by straight lines when plotted in $\log P$ and $1/T$ co-ordinates. This is seen from Fig. 3, in which by way of comparison there are plotted the experimental points for solutions containing 19.6 and 45.3 mol percentages of C_2H_5Cl .

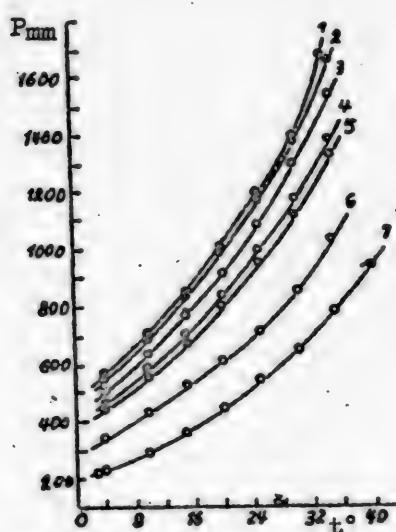


Fig. 2 Vapor pressure of solutions as a function of temperature.

1-100% C_2H_5Cl ; 2-92% C_2H_5Cl ; 3-70% C_2H_5Cl :
4-52.1% C_2H_5Cl ; 5-45.3% C_2H_5Cl :
6-19.6% C_2H_5Cl ; 7-100% $C_2H_5OC_2H_5$.

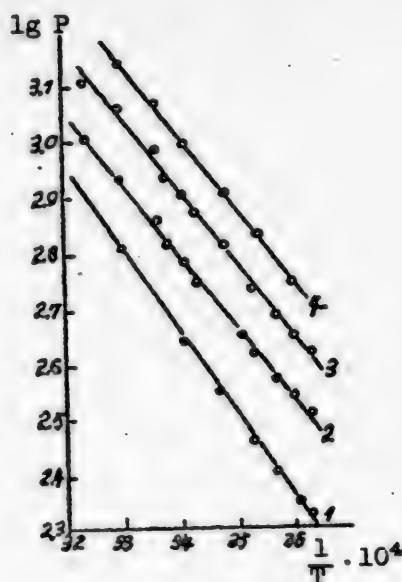


Fig. 3 Vapor pressure as a function of temperature in $\lg P$ and $1/T$ co-ordinates.

1-100% $C_2H_5OC_2H_5$; 2-19.6% C_2H_5Cl :
3-45.3% C_2H_5Cl ; 4-100% C_2H_5Cl .

In Table 4 the values of λ are shown for the solutions and pure components investigated by us.

TABLE 4

Values of λ For Solutions of $C_2H_5OC_2H_5 + C_2H_5Cl$

Mol.% of C_2H_5Cl	0	19.6	45.3	52.1	70.0	92	100
cal/mole....	6800	5900	5900	6000	5900	6000	5950

As is seen from Table 4, the quantity λ remains practically constant for all solutions containing from 19 to 100 molar per cent of C_2H_5Cl , equalling the molecular heat of vaporization of ethyl chloride.

c) Vapor Pressure as a Function of Solution Composition

The data for the vapor pressure of the solutions investigated by us at temperatures of 4, 10, 15, 20, 25, 30 and 34° are listed in Table 5; they were obtained by graphic interpolation.

As is seen in Table 5, at all temperatures the vapor pressure of the solutions increases regularly with an increase in the percentage of the more volatile component: ethyl chloride. In every case, the curve of vapor pressure as a function of the solution concentration departs in a positive direction from the straight line computed according to the principle of additivity.

TABLE 5
Variation of the Vapor Pressure of Solutions of $C_2H_5OC_2H_5 + C_2H_5Cl$
With Their Composition

Mol.% of C_2H_5Cl	Vapor Pressure in mm						
	4°	10°	15°	20°	25°	30°	34°
0.....	225	290	362	445	539	649	748
19.6...	341	427	512	613	750	871	997
45.3	441	560	666	803	967	1130	1266
52.1	457	582	700	835	1004	1182	1320
70.0	505	635	765	900	1075	1278	1460
92.0	542	689	822	987	1150	1360	1590
100.0	552	700	837	1000	1162	1381	1625

d) Composition of the Solution Vapor.

With the value of the total vapor pressure of the solutions, P , determined by us as a basis, we can compute P_1 , the partial vapor pressure of ethyl chloride, and P_2 , the partial pressure of diethyl ether. According to Dalton's law:

$$P_1 + P_2 = P. \quad (3)$$

Let us assume, with Margules [8], that:

$$P_1 = P_1^0 x_1 e^{\frac{a_2}{2}(1-x_1)^2 + \frac{a_3}{3}(1-x_1)^3}, \quad (4)$$

$$P_2 = P_2^0 (1-x_1) e^{\frac{\beta_2}{2} x_1^2 + \frac{\beta_3}{3} x_1^3}. \quad (5)$$

where P_1 and P_2 are the vapor pressures of pure C_2H_5Cl and $C_2H_5OC_2H_5$, respectively, and x_1 is the molar percentage of C_2H_5Cl in the solution.

The relationship between the coefficients a_2 , a_3 , β_2 and β_3 can be established by making use of the Duhem formula:

$$\frac{d \ln P_1}{d \ln x_1} = \frac{d \ln P_2}{d \ln(1-x_1)}, \quad (6)$$

with

$$\beta_2 = a_2 + a_3, \quad (7)$$

$$\beta_3 = -a_3. \quad (8)$$

The value of P , the total vapor pressure, may be obtained by adding Equations (4) and (5). Computing $\frac{dP}{dx_1}$ for $x_1 = 0$ and $x_1 = 1$, it is easy to derive the equation:

$$\frac{a_2}{2} + \frac{a_3}{3} = \ln \left\{ \left(\frac{dP}{dx_1} \right)_{x_1=0} + P_2^0 \right\} - \ln P_1^0, \quad (9)$$

$$\frac{\beta_2}{2} + \frac{\beta_3}{3} = \frac{a_2}{2} + \frac{a_3}{6} = \ln \left\{ P_1^0 - \left(\frac{dP}{dx_1} \right)_{x_1=1} \right\} - \ln P_2^0 . \quad (10)$$

By employing these equations it is easy to compute a_2 and a_3 , if the value of the derivative $\frac{dP}{dx_1}$ is first found for $x_1 = 0$ and $x_1 = 1$.

The simplest way of solving the latter problem is to select an empirical formula that describes the course of the function $P = f(x_1)$ in the vicinity of $x_1 = 0$ and $x_1 = 1$.

We made use of an empirical formula of the type

$$P = P_2^0 + ax + bx^2 . \quad (11)$$

Substituting two values P' and P'' in Equation (11) for two points x_2 and x_3 adjacent to $x = 0$, we get the following system of equations:

$$ax_2 + bx_2^2 = P^I - P_2^0 , \quad (12)$$

$$ax_3 + bx_3^2 = P^{II} - P_2^0 . \quad (13)$$

Solving this system, it is easy to find:

$$a = \left(\frac{dP}{dx_1} \right)_{x_1=0} = \frac{\begin{vmatrix} P^I - P_2^0 & x_2^2 \\ P^{II} - P_2^0 & x_3^2 \end{vmatrix}}{\begin{vmatrix} x_2 & x_2^2 \\ x_3 & x_3^2 \end{vmatrix}} \quad (14)$$

TABLE 6

Partial Vapor Pressures of C_2H_5Cl and $C_2H_5OC_2H_5$, in mm at $T = 4^\circ$

$$\frac{a_2}{2} = 0.8495; \quad \frac{a_3}{3} = 0.378; \quad \frac{\beta_2}{2} = 0.2825; \quad \frac{\beta_3}{3} = 0.378;$$

x_1	$P_1 = P_1^0 x_1 e^{-F(x_1)}$	$P_2 = P_2^0 (1 - x_1) e^{-F(x_1)}$	$P_1 + P_2$	$P_{\text{exper.}}$
0.196	154	188	342	341
0.453	304	136	440	441
0.520	335	123	458	457
0.700	411	88	499	505
0.920	512	31	543	542

We get the system of equations:

$$p(1 - x_4) + q(1 - x_4)^2 = P^{III} - P_1^0 , \quad (15)$$

$$p(1 - x_5) + q(1 - x_5)^2 = P^{IV} - P_1^0 , \quad (16)$$

for the region in the vicinity of $x = 1$ by a similar method.

Whence:

$$P = - \left(\frac{dp}{dx_1} \right)_{x_1=1} = \frac{\begin{vmatrix} P_{III}^o - P_1^o & (1-x_4)^2 \\ P_{IV}^o - P_1^o & (1-x_5)^2 \end{vmatrix}}{\begin{vmatrix} 1-x_4 & (1-x_4)^2 \\ 1-x_5 & (1-x_5)^2 \end{vmatrix}} \quad (17)$$

Using the figures for the vapor pressure of the solutions examined by us at $T = 4^\circ$, shown in Table 5, we found

$$\left(\frac{dp}{dx_1} \right)_{x_1=1} = 660 \text{ and } \left(\frac{dp}{dx_1} \right)_{x_1=1} = 113.5$$

with the aid of Equations (14) and (17).

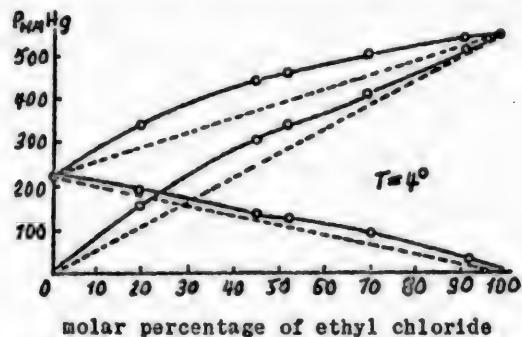


Fig. 4 Total and partial vapor pressure of the solutions of $C_2H_5Cl + C_2H_5OC_2H_5$ at 4°

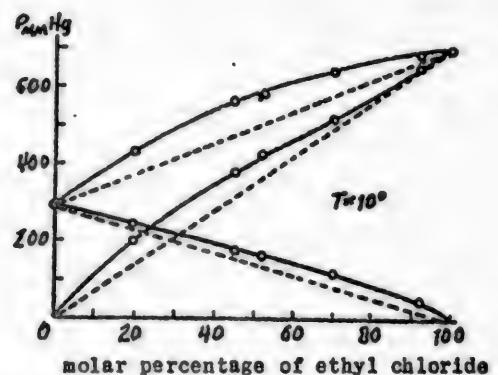


Fig. 5 Total and partial vapor pressure of the solutions of $C_2H_5Cl + C_2H_5OC_2H_5$ at 10°

Substituting these values in Equations (9) and (10), we found the values of the coefficients α_2 and α_3 and, with the aid of Equations (7) and (8), computed the coefficients β_2 and β_3 . Knowing these coefficients, we can easily compute the partial vapor pressures P_1 and P_2 for the solutions $C_2H_5OC_2H_5 + C_2H_5Cl$. The results of these computations for the isotherm $T = 4^\circ$ are listed in Table 6.

Table 7
Partial Vapor Pressures of C_2H_5Cl and $C_2H_5OC_2H_5$, in mm,
at the Temperatures of 10, 15, and 20°.

x_1	10°		15°		20°	
	P_1	P_2	P_1	P_2	P_1	P_2
0.196	195	240	216	303	250	371
0.453	379	174	452	210	527	258
0.520	418	160	502	191	589	233
0.700	517	114	625	135	740	161
0.920	647	49	772	47	923	52

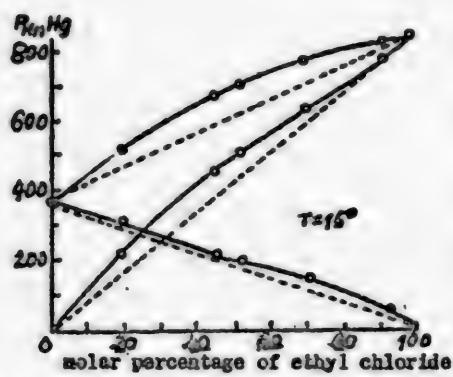


Fig. 6 Total and partial vapor pressures of the solutions $C_2H_5Cl + C_2H_5OC_2H_5$ at 15°

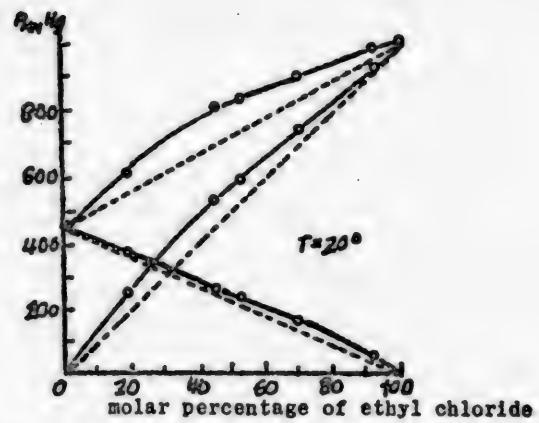


Fig. 7 Total and partial vapor pressures of the solutions $C_2H_5Cl + C_2H_5OC_2H_5$ at 20°

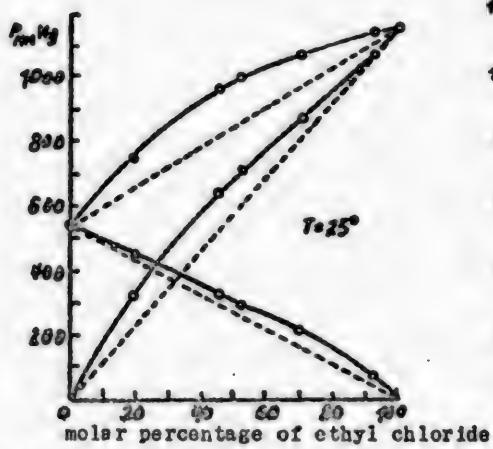


Fig. 8 Total and partial vapor pressures of the solutions $C_2H_5Cl + C_2H_5OC_2H_5$ at 25°

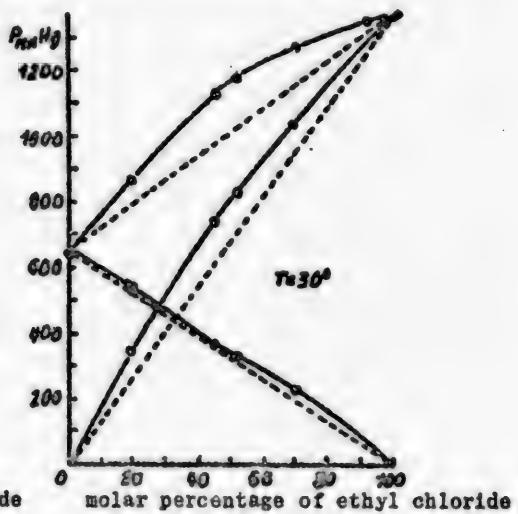


Fig. 9 Total and partial vapor pressures of the solutions $C_2H_5Cl + C_2H_5OC_2H_5$ at 30°

TABLE 8

Partial Vapor Pressures of C_2H_5Cl and $C_2H_5OC_2H_5$, in mm,
at the Temperatures of 25, 30, and 34°

x_1	25°		30°		34°	
	P ₁	P ₂	P ₁	P ₂	P ₁	P ₂
0.196	323	453	345	535	396	619
0.453	642	321	750	370	848	429
0.520	711	292	835	337	948	384
0.700	877	210	1040	230	1199	265
0.920	1072	75	1284	70	1498	88

As is seen in Table 6, the sum of the values P_1 and P_2 computed by us practically coincide with the value of the total vapor pressure P_{exper} . The curves of total and partial vapor pressures of the mixtures



are shown in Fig. 4.

Analogous computations were made by us for a number of other temperatures. The results of the computations for the temperatures 10, 15, and 20° are shown in Table 7, and in Table 8 for the temperatures 25, 30, and 34°.

In every instance the sums of the quantities P_1 and P_2 computed by us are equal to the total vapor pressure P_{exper} within the limits of experimental error.

These computations enabled us to construct curves of the variation of the partial vapor pressures of $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ with the composition of the solutions. These curves are given in Figs.

5-10.

As indicated in these graphs, at all temperatures the curves of total and partial vapor pressures are somewhat higher than the dotted straight lines plotted in accordance with the law governing ideal solutions. In every case the vapor is richer in the more volatile component than is the solution that is in equilibrium with it.

CONCLUSIONS

1. The total vapor pressure was determined for mixtures of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{Cl}$ of various concentrations in the temperature range 4-34°.

2. The partial vapor pressures were computed for solutions of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{Cl}$ at a number of temperatures.

3. It was demonstrated that the vapor above solutions of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{Cl}$ is always richer in ethyl chloride than is the liquid with which it is in equilibrium.

4. It was demonstrated that ethyl ether does not form azeotropic mixtures with ethyl chloride, and the necessary data have been obtained for computing a number of theoretical plates required for rectifying mixtures of $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and $\text{C}_2\text{H}_5\text{Cl}$.

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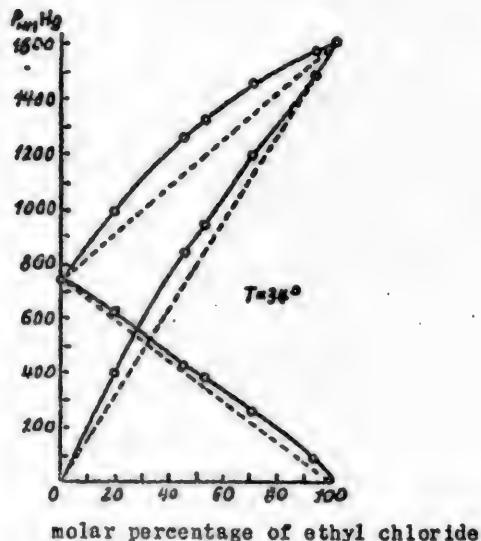


Fig. 10 Total and partial vapor pressures of the solutions $\text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ at 34°

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DOUBLE DECOMPOSITION IN THE ABSENCE OF A SOLVENT
COMPLEX-COMPUND FORMATION, SOLID SOLUTIONS, AND DOUBLE DECOMPOSITION
IN MELTS OF STRONTIUM AND BARIUM FLUORIDES AND CHLORIDES

A. G. Bergman and G. A. Bukhalova

GENERAL

Interrelated systems of fluorides and chlorides provide new and extremely interesting material in the field of the chemistry of molten salts, owing to their marked complex formation.

Fluorides are formed almost equally as anionic or cationic complexes, though as a rule the cationic complex predominates in most salts.

The most sharply marked 1:1 anionic complexes are formed by the chlorides

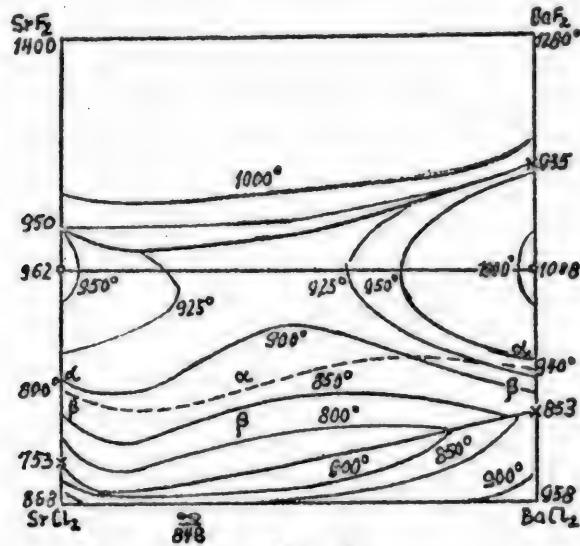


Fig. 1

and fluorides of the alkali earth metals: $\text{BaF}_2 \cdot \text{BaCl}_2$ (55% on the projection of the binary system $\text{BaF}_2 - \text{BaCl}_2$ in Fig. 2); somewhat less marked is the compound formed by SrF_2 and SrCl_2 (50% on the projection of the $\text{SrF}_2 - \text{SrCl}_2$ system in Fig. 2);

while CaF_2 and CaCl_2 form an incongruent compound (23% on the projection of the binary system).

Among the fluoride-chloride systems we notice an extremely large range of thermic effects of the exchange reaction (from 0.35 cal to 47 cal per gram equivalent), and as a result we have a wide gamut of different systems from the inversely reciprocal to the sharply singular, the latter exhibiting stratification only for exceptionally high thermic effects of the reaction.

The nature of the Sr, Ba, F, Cl systems investigated by us is governed by three factors: 1 - double decomposition; 2 - complex formation; and 3 - solid solutions.

As is evident from the fusibility diagram of the binary system $\text{SrCl}_2 - \text{BaCl}_2$, the fusibility diagram of the complex compounds $\text{SrCl}_2 \cdot \text{SrF}_2$ and $\text{BaCl}_2 \cdot \text{BaF}_2$, and the projection of the crystallization surface upon the square base (Fig. 1), the fluorides SrF_2 and BaF_2 , the chlorides SrCl_2 and BaCl_2 (Fig. 2), and the compounds $\text{SrCl}_2 \cdot \text{SrF}_2$ and $\text{BaCl}_2 \cdot \text{BaF}_2$ (Fig. 3) all produce continuous series of solid solutions.

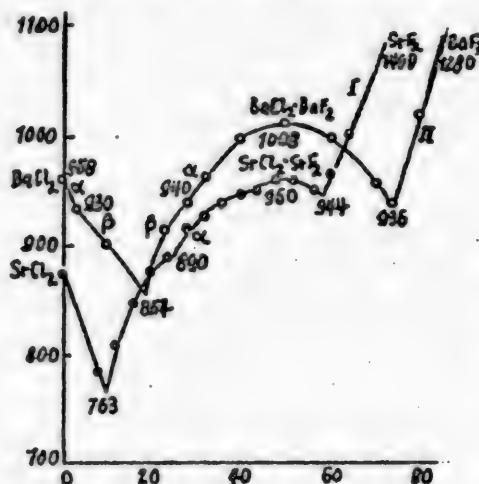


Fig. 2
Binary systems -
I - $\text{SrCl}_2 \cdot \text{SrF}_2$; II - $\text{BaCl}_2 \cdot \text{BaF}_2$

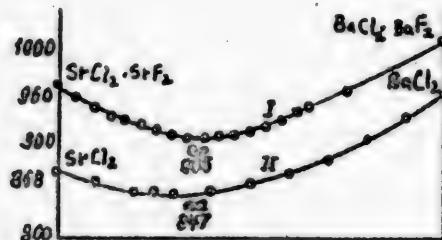


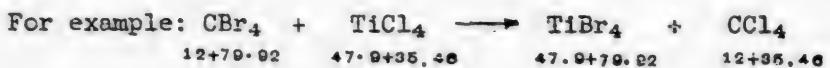
Fig. 3

The thermic effect of the reaction:



is 4.6 cal per gram equivalent.

The stable diagonal is the diagonal $\text{SrF}_2 - \text{BaCl}_2$ (Fig. 4), which agrees with the Gustavson-Beketov rule [1,2,3,4] that when two binary systems react with each other, the reaction proceeds in such a direction as to form compounds of the larger atoms with the larger atoms, and the smaller atoms with the smaller.



This also holds true in the double decomposition of molten salts of metals of the major subgroups. At the present time this assumption may also be extended to ionic radii.

If we consider ionic radii, the sum of the ionic radii of the SrF_2 molecule is 3.93 Å ($1.27 + 2 \times 1.33$), while it is 5.05 Å ($1.43 + 2 \times 1.81$) for BaCl_2 . Owing to the considerable difference between the sums of the conventional ionic radii in the molecular space, we might expect that the binary eutectic system $\text{SrF}_2 - \text{BaCl}_2$ would be formed, or, what is less likely, the compound $\text{SrF}_2 \cdot \text{BaCl}_2$. Experimental research into reciprocal systems containing anion complexes indicates that no such heterocompounds have been observed as yet in fluoride-chloride systems.

As was pointed out above, in the system investigated by us the stable diagonal ought to be the $\text{SrF}_2 - \text{BaCl}_2$ diagonal (Fig. 4), but the only slight bends in the isotherms and the curvature of the fields of crystallization (Fig. 1) indicate a slight shift of the double-decomposition fusion reaction toward the formation of stable components. In this system the tendency toward complex formation clearly predominates over the decomposition tendency.

When the $\text{Pb}, \text{Tl} \parallel \text{Cl}, \text{Br}$ [6] system is completely reversible, all three compounds at opposite sides form three series of continuous solid solutions with one another.

In the system of potassium and sodium fluorides and sulfates [5], on the other hand, the irreversible shift of the exchange reaction predominates, the fields of the isomeric compounds $\text{KF} \cdot \text{K}_2\text{SO}_4$ and $\text{NaF} \cdot \text{Na}_2\text{SO}_4$ do not meet — they are separated by the stable diagonal.

In our study of this system we established the fact that on the branches of the fusibility curve the compounds are transformed into the binary systems $\text{SrCl}_2 - \text{SrF}_2$ and $\text{BaCl}_2 - \text{BaF}_2$, which were not previously noticed in the work done by Plato [12], who employed thermal analysis. These transformations are also manifested in the corresponding area of the crystallization of solid solutions of complexes. As is seen in the projection, the transformation curve (Fig. 1 and 7), possesses a minimum. These conversions must, apparently, be related to the number of homeomorphic crystal lattices, i.e., established without marked rearrangement [87].

It is extremely significant that the homeomorphic transformations of the compound $\text{SrF}_2 \cdot \text{SrCl}_2$ was also observed by us in the $\text{Na}, \text{Sr} \parallel \text{F}, \text{Cl}$ system, where there are no solid solutions and where the transformation temperature is lowered, crossing the isotherm. If the conversion were heteromorphous, the curve of polymorphic transformations should follow the isotherm when no solid solutions exist.

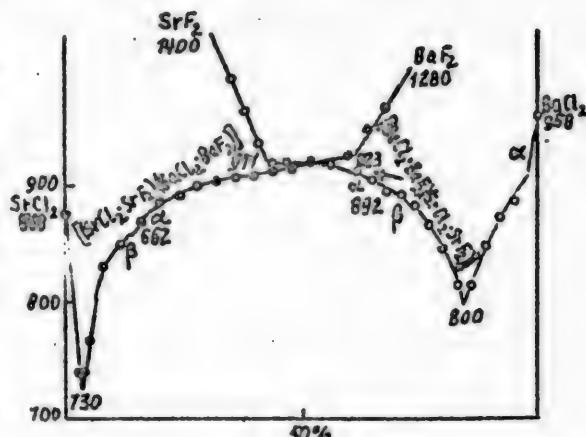


Fig. 4

—●— Diagonal section $\text{SrCl}_2 - \text{BaF}_2$
○—○— Diagonal section $\text{BaCl}_2 - \text{SrF}_2$

EXPERIMENTAL SECTION

Methods

Determinations were made by the visual-polythermal method in a platinum crucible with a platinum stirrer, placed in an electric furnace at 1200°. The interior of the furnace was illuminated by a powerful reflector bulb to compensate for the furnace's own light. The thermocouple was of the platinum - platinum - rhodium type, and the indicating instrument was a sensitive Siemens-Halske millivoltmeter. The raw materials were carefully prepared and purified. The fluorides of Sr and Ba were synthesized from double-distilled hydrofluoric acid and freshly precipitated carbonates, which were, in turn, prepared from recrystallized chlorides.

The melting points adopted for the pure components were as follows: BaF_2 - 1289°, SrF_2 - 1400°, BaCl_2 - 958°, and SrCl_2 - 888°. BaCl_2 undergoes a heteromorphous transformation at 930°. All composition data are expressed in molecular percentages.

Binary Systems

1. $\text{SrCl}_2 - \text{BaCl}_2$ (Fig. 3, Table 1) has been studied by Ruff and Plato [8], Sandonini [10], and Vortisch [11]. The temperatures determined by us for the three percentages 25, 50, and 70% are in good agreement with the cited data. The minimum on the continuous curve of solid solutions corresponds to 840° and 30% BaCl_2 .

2. $\text{SrF}_2 - \text{BaF}_2$ was not investigated by us, owing to the high temperatures involved; it may be assumed that the curve represents solid solutions with a minimum, since in the analogous system $\text{CaF}_2 - \text{BaF}_2$ investigated by us, we have continuous solid solutions with a minimum. This is all the more evident since the difference between the ionic radii of strontium and barium is smaller than for barium and calcium (ionic radii: Ca - 1.06 Å, Sr - 1.27 Å, Ba - 1.43 Å).

3. $\text{SrF}_2 - \text{SrCl}_2$ (Fig. 2, Table 1) was investigated by Plato [12] and by Winter [13]. According to Plato's data, the melting point of the congruent compound $\text{SrCl}_2 \cdot \text{SrF}_2$ is 962°, and that of the eutectic: 1) 753° - 13% SrF_2 ; 2) 962° - 63% SrF_2 . This system was repeated by us and generally confirmed; moreover, we found a homeomorphic transformation in the branch of the compound $\text{SrCl}_2 \cdot \text{SrF}_2$ at 890° and 25.5% SrF_2 .

4. $\text{BaCl}_2 - \text{BaF}_2$ (Fig. 2, Table 1) was investigated by the same authors [12, 13]. Our results differ only in the presence of a point of homeomorphic transformation at 940° and 29% BaF_2 along the branch of the compound $\text{BaCl}_2 \cdot \text{BaF}_2$.

The eutectic points are 854°, 19% BaF_2 ; and 936°, 73.5% BaF_2 . The melting point of the compound $\text{BaCl}_2 \cdot \text{BaF}_2$ is 1008°.

5. $\text{SrF}_2 \cdot \text{SrCl}_2 - \text{BaF}_2 \cdot \text{BaCl}_2$ — cross section V has the character of a binary system (Fig. 3, Table 5). The minimum on the continuous solid-solution curve corresponds to 906° and 36% $\text{BaCl}_2 \cdot \text{BaF}_2$.

TABLE 1

Binary Systems

SrCl ₂ - BaCl ₂			BaCl ₂ - BaF ₂			SrCl ₂ - SrF ₂		
No.	Mol. % BaCl ₂	Temper-ature	No.	Mol. % BaF ₂	Tempera-ture	No.	Mol. % SrF ₂	Tempera-ture
1	0	870°	1	0	958°	1	0	860°
2	10	860	2	3.5	930°	2	8	784
3	20	850	3	10	900	3	12	806
4	30	847	4	20	876	4	16	846
5	40	850	5	24	912	5	20	877
6	50	860	6	28	936	6	24	888
7	60	870	7	32	960	7	28	913
8	70	885	8	40	984	8	32	924
9	80	905	9	50	1008	9	36	937
10	90	930	10	60	996	10	40	944
11	100	955	11	70	955	11	44	948
—	—	—	12	73.5	936	12	48	958
—	—	—	13	80	1018	13	52	958
—	—	—	—	—	—	14	56	950
—	—	—	—	—	—	15	60	963
—	—	—	—	—	—	16	64	1000

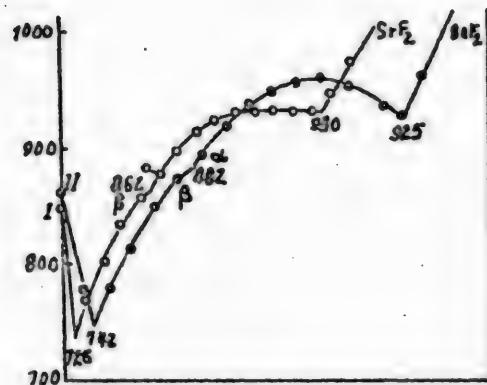


Fig. 5
Binary systems: I-(25% BaCl₂, 75% SrCl₂) → SrF₂,
II-(50% BaCl₂, 50% SrCl₂) → BaF₂

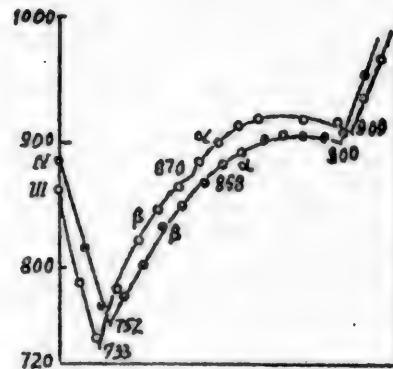


Fig. 6
III-(50% BaCl₂+50% SrCl₂) → SrF₂,
IV -(70% BaCl₂+30% SrCl₂) → SrF₂

Cross Sections

We investigated two diagonals and five internal cross sections (Figs. 3, 4, 5, 6) to ascertain the surface of crystallization.

TABLE 2

Diagonal cross section $\text{SrCl}_2 - \text{BaF}_2$			Diagonal cross section $\text{BaCl}_2 - \text{SrF}_2$		
No.	Mol.% BaF_2	Tempera- ture	No.	Mol.% SrF_2	Tempera- ture
1	0	874°	1	0	958°
2	3	740	2	5	886
3	4	742	3	8	871
4	5	767	4	11	846
5	8	829	5	14	814
6	12	849	6	17	814
7	16	868	7	20	848
8	20	886	8	23	865
9	24	891	9	26	881
10	28	900	10	29	888
11	32	903	11	32	893
12	36	906	12	35	903
13	40	907	13	38	910
14	44	909	14	43	917
15	48	912	15	53	918
16	52	916	16	56	919
17	56	919	17	59	934
18	60	923	18	62	963
19	64	947	19	65	989
20	68	965			

The diagonal cross section $\text{SrCl}_2 - \text{BaF}_2$ (Fig. 4, Table 2) consists of four branches:

1 - Solid solutions of strontium and barium chlorides;

2 - α and β homeomorphic modifications of the solid solutions $(\text{SrCl}_2 \cdot \text{SrF}_2) \cdot (\text{BaCl}_2 \cdot \text{BaF}_2)$ and

3 - Solid solutions of strontium and barium fluorides; the ends of the branches correspond to: 730° and 3.5% BaF_2 ; 662° and 15% BaF_2 ; and 923° and 62% BaF_2 .

The diagonal cross section $\text{BaCl}_2 - \text{SrF}_2$ (Table 2, Fig. 4) likewise consists of four branches:

1 - The branch of strontium and barium fluorides;

2- and 3 - α and β homeomorphic modifications of the solid solutions $(\text{BaCl}_2 \cdot \text{BaF}_2) \cdot (\text{SrCl}_2 \cdot \text{SrF}_2)$;

4 - Solid solutions of the fluorides of strontium and barium, intersecting at 800° and 15.5% SrF_2 ; 890° and 31.5% SrF_2 ; and 917° and 57% SrF_2 .

TABLE 3

Cross Section I			Cross Section II		
25% BaCl ₂ } → SrF ₂		50% BaCl ₂ } → BaF ₂		50% SrCl ₂ } → BaF ₂	
No.	Mol. % SrF ₂	Tempera-ture	No.	Mol. % BaF ₂	Tempera-ture
1	0	850°	1	0	860°
2	2	777	2	5	777
3	5	770	3	10	778
4	9	802	4	15	813
5	13	834	5	20	850
6	17	857	6	25	873
7	21	877	7	30	894
8	25	887	8	35	917
9	29	913	9	40	937
10	33	923	10	45	947
11	37	930	11	50	954
12	41	930	12	55	957
13	45	930	13	61	951
14	49	930	14	68	934
15	53	930	15	72	925
16	57	945	16	76	958
17	61	970	-	-	-

Points of intersection:

1 - 726° 2.5% SrF₂,
 2 - 852 29 SrF₂,
 3 - 930 55 SrF₂.

Points of intersection:

1 - 742° 6.5% BaF₂,
 2 - 882 28 BaF₂,
 3 - 925 72 BaF₂.

TABLE 4

Cross Section III			Cross Section IV		
50% BaCl ₂ } → SrF ₂		70% BaCl ₂ } → SrF ₂		30% SrCl } → SrF ₂	
No.	Mol. % SrF ₂	Tempera-ture	No.	Mol. % SrF ₂	Tempera-ture
1	0	860°	1	0	883°
2	4	785	2	5	814
3	8	740	3	9	766
4	12	779	4	13	773
5	16	819	5	17	800
6	20	844	6	21	830
7	24	862	7	25	847
8	28	882	8	29	865
9	32	898	9	33	880
10	36	912	10	37	891
11	40	918	11	41	899
12	49	918	12	45	903
13	56	914	13	49	905
14	61	933	14	53	903
15	64	967	15	57	907
-	-	-	16	61	955

Points of Intersection:

1 733° 8.5% SrF₂,
 2 870 26 SrF₂,
 3 909 59 SrF₂.

Points of Intersection

1 752° 10% SrF₂,
 2 868 31 SrF₂,
 3 900 56 SrF₂.

Cross Section V

A [50% SrF₂ + 50% SrCl₂] → B [50% BaF₂ + 50% BaCl₂]

No.	Mol.% B	Tempera- ture	No.	Mol.% B	Tempera- ture	No.	Mol.% B	Tempera- ture
1	0	960°	7	26	914°	13	50	913°
2	5	947	8	30	908	14	54	919
3	10	939	9	34	906	15	58	925
4	14	929	10	38	906	16	62	933
5	18	923	11	42	909	17	65	940
6	22	921	12	46	911	18	75	956
						19	100	1008

Cross Sections I, II, III, and IV are like diagonal cross sections (cf. Figs. 5 and 6, Tables 3 and 4).

Reciprocal Systems Sr, Ba || F, Cl

The crystallization surface of the system has been constructed (Photographs 1a, 1b) from the four binary systems, the two diagonal cross sections and the four internal cross sections.



Photo 1a



Photo 1b

The surface of crystallization consists of four principal areas:

- 1) Solid solutions of the chlorides of strontium and barium;
- 2) Solid solutions of the fluorides of strontium and barium;

3 - An area of a continuous solid solution of two anionic complexes, $\text{SrCl}_2 \cdot \text{SrF}_2$ and $\text{BaCl}_2 \cdot \text{BaF}_2$, subdivided into two areas α and β of homeomorphic varieties.

The nature of the curves separating the crystallization surfaces are quite visible in the system square in Fig. 1 and in the projection of the crystallization surface on the $\text{SrCl}_2 - \text{BaCl}_2$ face (Fig. 7).

There is a minimum at 903° and 30% BaCl_2 , 51% SrF_2 , 19% SrCl_2 on the curve separating the area of fluoride solid solutions from the α form of double salts. On the curve separating the homeomorphic varieties α and β the minimum is at 866° and 32% BaCl_2 , 23% SrF_2 , 45% SrCl_2 .

The curve separating the chloride solid solutions and the homeomorphic modifications of solid solutions of the compounds has a minimum at 725° and 20% BaCl_2 , 3% SrF_2 and 77% SrCl_2 .

The crystallization surface of the solid solutions $\text{SrCl}_2 \cdot \text{SrF}_2$ and $\text{BaCl}_2 \cdot \text{BaF}_2$ is saddle-shaped. The area of the square is distributed as follows among the four areas: 1 - solid solutions of the fluorides occupies 38.8%; 2 - solid solutions of compounds, 52.6%; and 3 - solid solutions of chlorides, 8.6%.

CONCLUSIONS

Despite the rather high thermal effect of the exchange reaction, 4.6 Cal per gram equivalent, the diagonal $\text{BaCl}_2 - \text{SrF}_2$, which is stable with respect to the thermal effect of the exchange, is not manifested by any geometrical elements on the system's crystallization surface; it is absent, as a general thing, from the system. Evidently, the magnitude of the thermal effect of compound formation is greater than the thermal effect of the double decomposition reaction, for if this were not so, a sharp shift of the exchange reaction toward the $\text{SrF}_2 - \text{BaCl}_2$ side should produce a eutectic system along the stable diagonal, for the sums of the ionic radii of the stable components, 3.95 Å and 5.05 Å, are markedly different, to get a continuous series of solid solutions. At the same time this excludes the formation of hetero-compounds.

On the basis of the investigation of a large number of reciprocal systems of fluorides and chlorides with salts of strontium and barium (which will be discussed in subsequent papers), the heats of formation of the compounds could be determined as 9.8 ± 1.1 cal for $\text{SrF}_2 \cdot \text{SrCl}_2$ and 12.0 ± 1 cal for $\text{BaF}_2 \cdot \text{BaCl}_2$.

The initial division of the square of a reciprocal system into phase triangles does not take place in our system, wherein it differs from most of the systems investigated previously. The square is divided by stable secants connecting constituents of both compounds that lie on opposite sides of the square; the same is divided into two quadrangles - two rectangles - in neither of which are

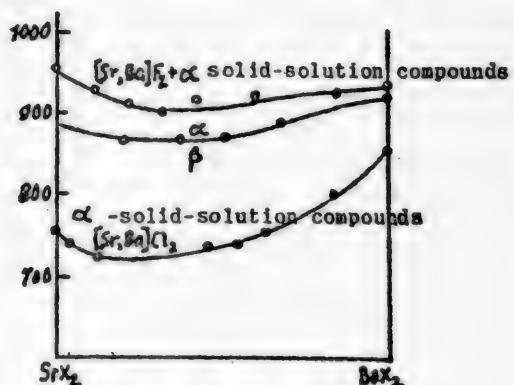
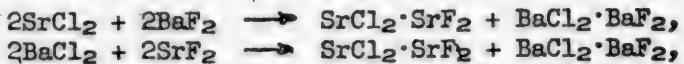


Fig. 7
Projection of $\text{Sr}, \text{Ba} \parallel \text{F}, \text{Cl}$
on the $\text{SrCl}_2 - \text{BaCl}_2$ face.

we any more able to draw stable diagonals.

The reaction equations:



serve to determine the point of intersection of the diagonals. The compounds obtained in both reactions form continuous series of solid solutions.

SUMMARY

1. The crystallization surface of a ternary reciprocal system of the fluorides and chlorides of strontium and barium Sr, Ba || F, Cl was investigated by the method of visual-polythermal analysis.

2. Stable anionic complexes $\text{SrCl}_2 \cdot \text{SrF}_2$ and $\text{BaCl}_2 \cdot \text{BaF}_2$, melting congruently at 960° and 1008° , are formed between the fluorides and chlorides of corresponding metals; homeomorphic transformations were established for both compounds at 890° and 940° , respectively.

3. Owing to the formation of a continuous series of solid solutions between the chlorides of Sr and Ba, their fluorides, and the corresponding α and β forms of anionic complexes, the liquidus surface consists of four surfaces of crystallization separated by curves of joint crystallization of two series of solid solutions.

4. Owing to the comparatively small thermal effect of double decomposition, 4.6 Cal, in the direction of $\text{BaCl}_2 - \text{SrF}_2$ pair, and owing to the marked complex formation, the stable diagonal $\text{BaCl}_2 - \text{SrF}_2$ does not appear at all. The square is not subdivided along the diagonal, but along secants, connecting the peaks of both compounds, into two phase quadrangles (rectangles), in each of which the solidified melts consist of two kinds of crystals of the respective series of solid solutions.

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SPECTROPHOTOMETRIC INVESTIGATION OF COBALT-CHLORIDE AND COBALT-BROMIDE COMPLEXES IN ACETONE

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The absorption of acetone solutions of cobalt chloride and bromide has been investigated by a number of authors [1]. In these solutions a characteristic increased absorption is observed in the spectral region of 600-700 m μ , similar to that observed in aqueous solutions of CoCl_2 and CoBr_2 in the presence of HCl and HBr or their salts [2]. The increased absorption in this portion of the spectrum is ascribed by some authors to a diminished solvation of the cobalt ions, whereas other authors consider the cause of this phenomenon to be the formation of complex groups, the most probable constitutions of which being CoCl_4^{--} and CoBr_4^{--} .

In one of our previous papers [3] we investigated the systems $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ and $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$ in acetone by the method of continuous variations, which is a special application to research on complex groups in solutions of the constitution - property diagram developed by N. S. Kurnakovskiy [4]. The optical density of the solutions was used as the property investigated, [5].

We established the existence of these complexes in 0.01 molar solutions, the cobalt/chlorine ratio being 1:4. The simplest composition of such complexes is CoCl_4^{--} and CoBr_4^{--} ; the method of continuous variations is unable, however, to establish whether these complexes exist in the solution in their simplest form of CoCl_4^{--} and CoBr_4^{--} or in the more complicated forms: $\text{Co}_2\text{Cl}_8^{----}$, $\text{Co}_2\text{Br}_8^{----}$ etc. To ascertain the degree of complexity of these complexes we investigated the systems $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ and $\text{Co}(\text{ClO}_4)_2 + \text{LiBr}$ in acetone by the method of terminal logarithms. The solution concentrations were the same as those used with the method of continuous variations. Experiments indicated the composition of the complexes from the component ratio, which was 1:4.

Method of Terminal Logarithms

In determining the composition of a complex formed in a solution in accordance with the equation:



the problem involved is determining m and n . In so doing, A, for example, may be the cation, while B is any molecule or anion. The following equation may be derived from the equation for the equilibrium constants of the system (1):

$$\log [\text{A}_m\text{B}_n] = m \log [\text{A}] + n \log [\text{B}] - \log k, \quad (2)$$

from which it follows that if the concentration of one of the components say A, is constant, while the concentration of the other component, in this case B, varies, the logarithm of the concentration of the complex, $\log [A_m B_n]$, will be a linear function of $\log [B]$. The quantity n denotes the value of the proportionality factor for the variation of $\log [A_m B_n]$ with changes in $\log [B]$.

If the optical density of the system is directly proportional to $[A_m B_n]$, the logarithm of optical density must be a linear function of $\log [B]$. When the values of $\log [B]$ and the logarithms of the corresponding optical densities $\log D$ are plotted on a graph with the co-ordinate system $\log [B] - \log D$, we should get a straight line, the slope of which corresponds to the value of n . (Fig. 1.).

The value of m for constant concentration of the component [B] may be determined by the same method. This method was employed by Bent and French in studying the composition of the complex ion $Fe(NS)^{++} [s]$ and by Babko in studying the iron-fluoride complex $FeF^{++} [7]$.

EXPERIMENTAL

Optical densities were measured with the Beckman photoelectric spectrophotometer, yielding results reproducible within 0.2%. The cobalt preparation used was $Co(ClO_4)_2 \cdot 6H_2O$, since the perchlorate does not form complexes with the cobalt ion [8]. The cobalt perchlorate was prepared from chemically pure cobalt carbonate, free from nickel, and chemically pure perchloric acid. The $Co(ClO_4)_2 \cdot 6H_2O$ was twice recrystallized before solutions were prepared. The acetone was purified and dessicated as described in the literature [9]. The chemically pure lithium chloride was obtained from lithium carbonate and hydrochloric acid. The LiCl was twice recrystallized and dried in a stream of nitrogen at 120° [10].

Cobalt-Chloride Complexes

A series of solutions with constant chlorine-ion concentrations and variable cobalt-ion concentrations was prepared to determine the number of cobalt ions entering into the composition of the complex. The optical density of the solutions was measured at $\lambda = 650 m\mu$, since this was the wavelength we had used for the same concentrations in finding the complex with a $\frac{m}{n} = 1:4$ ratio by the method of continuous variations.

The measured optical densities and the solution concentrations are listed in Table 1.

Figure 2 is a graphical representation in the co-ordinate system $\log [Co(ClO_4)_2] - \log D$. As may be seen from Fig. 2, $\frac{m}{n} = 1$, which indicates the presence of a single cobalt ion in the cobalt-chloride complex.

A series of solutions with concentrations at which the ratio $m/n = 1:4$ was found by the method of continuous variations was prepared to determine the number



Fig. 1 variation of $\log D$ with $\log [B]$

TABLE 1
Composition of Solutions and Their Optical Densities for Constant Value of
[LiCl] and Varying Concentrations of $\text{Co}(\text{ClO}_4)_2$

No.	Concentration moles/liter		D $\lambda = 650 \text{ m}\mu$	$\log D+1$	$\log[\text{Co}(\text{ClO}_4)_2]$	$\log[\text{Co}(\text{ClO}_4)_2] + 3.54777$
	$\text{Co}(\text{ClO}_4)_2$	LiCl				
1	0.001	0.002	0.353	0.54777	3.00000	0.54777
2	0.002	0.002	0.700	0.84510	3.30103	0.84880
3	0.003	0.002	1.000	1.00000	3.47712	1.02489
4	0.004	0.002	1.30	1.11394	3.60206	1.14983
5	0.005	0.002	1.54	1.18752	3.69897	1.24674
6	0.006	0.002	1.80	1.25527	3.77815	1.32592

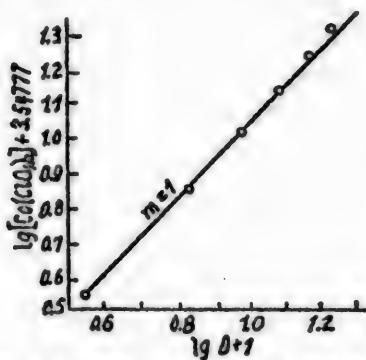


Fig. 2 Variation of $\log D$ with $\log [\text{Co}(\text{ClO}_4)_2]$ in the $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$ system.

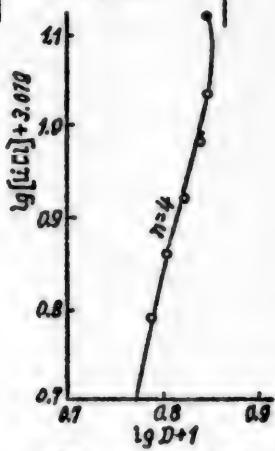


Fig. 3 Variation of $\log D$ with $\log [\text{LiCl}]$ in the $\text{Co}(\text{ClO}_4)_2 + \text{LiCl}$

of chlorine ions entering into the composition of the cobalt-chloride complex. Measurements were made at the wavelength of $650 \text{ m}\mu$.

The concentrations of the solutions and their optical densities are listed in Table 2. The graph $\log [B] - \log D$ is depicted in Fig. 3. The slope of the straight line in this case indicates that $n = 4$. Hence, there are four chlorine ions in the composition of the cobalt-chlorine complex.

Thus, the method of terminal logarithms corroborated the ratio $m/n = 1:4$ obtained by the method of continuous variations, proving that the cobalt-chlorine complex has the following composition: CoCl_4^{--} .

Cobalt-Bromide Complexes

The composition of the complexes was determined as described above. Chemically pure lithium bromide was prepared from lithium carbonate and hydrochloric acid. The LiBr, twice recrystallized, was dessicated in a current of nitrogen at

TABLE 2

Composition of Solutions and Their Optical Densities For Constant Values of $[Co(ClO_4)_2]$ and Varying Concentrations of LiCl

No.	Concentration moles/liter	D $\lambda = 650 \text{ m}\mu$	$\log D + 1$	$\log [LiCl]$	$\log [LiCl] +$ $+ 3.07918$
	$Co(ClO_4)_2$	LiCl			
1	0.002	0.005	0.600	0.77815	0.77815
2	0.002	0.006	0.630	0.80550	0.85733
3	0.002	0.007	0.680	0.83251	0.92242
4	0.002	0.008	0.710	0.85126	0.98227
5	0.002	0.009	0.715	0.85431	1.03432
6	0.002	0.011	0.710	0.85126	1.12057

a temperature of 160° [10]. The solution concentrations used and the wavelengths at which their optical densities were measured were the same as those for which we obtained the ratio $m/n = 1:4$ by the method of continuous variations. The

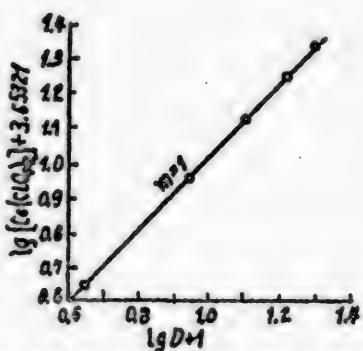


Fig. 4 Variation of $\log D$ with $\log [Co(ClO_4)_2]$ in the $Co(ClO_4)_2 + LiBr$.

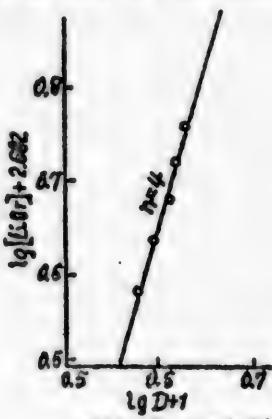


Fig. 5 Variation of $\log D$ with $\log [LiBr]$ in the $Co(ClO_4)_2 + LiBr$.

cobalt-ion content was determined by investigating solutions of $Co(ClO_4)_2 + LiBr$ with a constant LiBr concentration and varying concentrations of $Co(ClO_4)_2$. The solution concentrations and optical densities of this series are listed in Table 3.

The graph of $\log [Co(ClO_4)_2] - \log D$, shown in Fig. 4, proves that $m = 1$. Thus, the solution contains mononuclear cobalt-chloride complexes.

Solutions with a constant concentration of $Co(ClO_4)_2$ and varying concentrations of LiBr were prepared to determine the number of bromine ions in the complex. The constitution of the solutions and their optical densities are listed in Table 4. It follows from Fig. 5, where the function $\log [LiBr] - \log D$ is plotted, that $n = 4$.

TABLE 3

Composition of Solutions and Their Optical Densities for Constant Value of [LiBr] and Varying Concentrations of $\text{Co}(\text{ClO}_4)_2$

No.	Concentration moles/liter		$D_{\lambda=675 \text{ m}\mu}$	$\log D+1$	$\log [\text{Co}(\text{ClO}_4)_2]$	$\log [\text{Co}(\text{ClO}_4)_2] + 3.65321$
	$\text{Co}(\text{ClO}_4)_2$	LiBr				
1	0.001	0.002	0.450	0.65321	3.00000	0.65321
2	0.002	0.002	0.885	0.94694	3.30103	0.95424
3	0.003	0.002	1.28	1.10721	3.47712	1.13033
4	0.004	0.002	1.70	1.23045	3.60206	1.25527
5	0.005	0.002	2.00	1.30103	3.69897	1.35218

TABLE 4

Composition of solutions and Their Optical Densities for Constant Value of $[\text{Co}(\text{ClO}_4)_2]$ and Varying Concentrations of LiBr

No	Concentration moles/liter		$D_{\lambda=725 \text{ m}\mu}$	$\log D+1$	$\log [\text{LiBr}]$	$\log [\text{LiBr}] + 2.68237$
	$\text{Co}(\text{ClO}_4)_2$	LiBr				
1	0.002	0.008	0.385	0.58546	3.90309	0.58546
2	0.002	0.009	0.390	0.59100	3.95424	0.63661
3	0.002	0.010	0.418	0.62118	2.00000	0.68237
4	0.002	0.011	0.425	0.62839	2.04139	0.72376
5	0.002	0.012	0.435	0.63839	2.07918	0.76155

Thus, the ratio $m/n = 1:4$ derived by us by the method of continuous variations is confirmed in this case as well. In this case, the cobalt-bromide complexes had the following cobalt and bromine composition: CoBr_4^{--} .

SUMMARY

1. In the solutions investigated by us by the method of terminal logarithms the presence of CoCl_4^{--} and CoBr_4^{--} complexes has been established.

2. The complex compositions found by the method of terminal logarithms corroborated the ratio $m/n = 1:4$, derived by us earlier for these complexes by the method of continuous variations.

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THERMOCHEMISTRY OF COMPLEX COBALT SALTS WITH NEUTRAL ADDITIVES

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The complex compounds of cobalt (III) with neutral additives have been the subject of very limited study from the thermochemical standpoint. The heats of formation and the heats of solution of three roseo salts, $[Co(NH_3)_5H_2O]Cl_3$, $[Co(NH_3)_5H_2O]Br_3$ and $[Co(NH_3)_5H_2O](NO_3)_3$ have been determined by Lamb and Simmons [1]. Blitz [2] determined the dissociation pressure of the luteochloride, but according to him the salt's heat of formation cannot be computed, as a mixture of various dissociation products is then formed. In general, the other groups of complex compounds of cobalt (III) have not been investigated thermochemically by anyone.

In an attempt to undertake the systematic study of the thermochemistry of complex cobalt salts, we decided to obtain data for the luteo salts, the roseo salts, and the diaquotetrammine and ethylene diamine salts.

To determine the heats of formation of these salts, the heat of reaction between the crystalline salt and a 0.26 molar solution of sodium sulfide was measured. This reaction proceeds in accordance with the following equation:



where A is any neutral addendum, and X is a single-charge anion.

The apparatus and the methods used in these determinations differed in no way from those described by us in our previous communication [3]. All determinations were made at 25°.

EXPERIMENTAL

The cobalt luteochloride was prepared and purified by the method described by Bjerrum [4]; the other luteo salts were prepared by the method described by Gibbs, Genth [5], and Jorgensen [6]. The roseochloride was prepared by the Rose method [7], and the roseoiodide by the method set forth by Ephraim, [8]. The diaquotetrammine chloride was prepared by the Jorgensen method [9]. The ethylene diamine salts were prepared by the methods outlined by Jorgensen [9] and Pfeiffer and Gassman [10].

The purity of the salts prepared was checked by making a chemical analysis for one of the components.

The heat of reaction with a 0.26 molar solution of Na_2S was determined for the luteochloride, luteobromide, luteoiodide, luteonitrate, roseoiodide, di-aquotetrammine chloride, triethylene diamine iodide, triethylene diamine nitrate, and roseochloride. The heat of reaction was determined by Lamb and Simmons [1] for the last-named salt, but their data do not agree with the heat of solution found by them for the very same salt. Computing the heat of formation of the roseochloride from the heat of reaction with a 0.26 molar solution of Na_2S , we get the value of 312.3 Cal; computing the same heat of formation of this salt from the heat of solution in water, we get 313.6 Cal. The existence of this discrepancy made it necessary to repeat the determinations of both the heat of reaction of roseochloride with Na_2S and its heat of solution in water.

The values obtained by us for the heat of reaction of the salts listed above with a solution of sodium sulfide are given in Table 1. The value of the heat of reaction for the roseochloride differs by 0.3 Cal from the value cited by Lamb and Simmons.

The heat of solution in water was determined for the following salts: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$, $[\text{Coen}_3]\text{I}_3$, and $[\text{Coen}_3](\text{NO}_3)_3$. The value of the heat of solution of the roseochloride found by us differs by 0.6 Cal. from the value found by Lamb and Simmons [1]. The heats of solution found by us are listed in Table 2.

The experimental data found by us can be used to compute both the heat of formation of complex solid salts in the standard state and the heat of formation of complex ions in aqueous solution. The heat of formation of solid salts was computed from the heat of reaction with a solution of sodium sulfide. The heats of formation of all the products taking part in this reaction and formed as a result of the reaction were taken from Thermochemistry, by Bichowsky and Rossini, [11]. The heats of formation of complex ions in aqueous solution were computed from the heats of formation of solid salts, their heats of solution, and the heats of formation of the anions in aqueous solution. In five instances the heats of formation of solid salts were also computed from their heats of solution in water and the heats of formation of the corresponding ions. The values thus obtained do not differ by more than 0.3 Cal from those computed earlier by another method.

Discussion of Results

The thermochemical data found by us for the complex salts of cobalt (III) with neutral additives make it possible to compare the thermal stability of various complex salts. Making this sort of comparison necessitates the "isolation" of the complex ions from the influence of ions located in the outer shell, i.e., to break down the overall effect of salt formation into quantities defining interactions within the complex ion and interactions between ions. Governed by these considerations, we shall compare the heats of formation of gaseous complex ions, employing the concept of the space-lattice energy of a complex salt [12] for computing them.

The heat of formation of a gaseous complex ion may be found from the equation:

$$-\Delta H_k = -\Delta H_{kA} + \Delta H_A - U_{kA} \quad (1)$$

TABLE 1

Heat of Reaction of Crystalline Salts with 0.26 Molar Solution of Na_2S

Formula of Salt	Weight g	Change in temperature in $^{\circ}\text{C}$, corrected for radiation	Radiation correction	Heat capacity of the calorimeter cal	Heat of reaction	Mean value of heat of reaction
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	0.9969	-0.030 ₈	-0.008	520.7	-4280	-4280
"	0.9945	-0.030 ₈	-0.007	520.8	-4290	
$[\text{Co}(\text{NH}_3)_6]\text{Br}_3$	0.9987	-0.036 ₇	+0.004	520.7	-7750	-7710
"	0.9987	-0.036 ₇	-0.008	520.8	-7670	
$[\text{Co}(\text{NH}_3)_6]\text{I}_3$	0.9988	-0.038	-0.008 ₄	520.9	-10740	-10700
"	0.9973	-0.037 ₇	-0.008	520.9	-10670	
$[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$...	1.0013	-0.072 ₃	-0.008	520.7	-13050	-13070
" ...	0.9892	-0.071 ₈	-0.005 ₃	520.7	-13080	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$..	0.9978	+0.043 ₈	-0.006	520.8	+6140	+6150
" ..	0.9942	+0.043 ₈	-0.005	520.9	+6160	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$..	0.9966	-0.003 ₃	-0.006 ₂	520.8	-936	-940
" ..	0.9861	-0.003 ₃	-0.003 ₂	520.7	-946	
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$..	0.9949	+0.051	-0.011	520.4	+7190	+7270
" ..	0.9925	+0.052	-0.006	520.9	+7350	
$[\text{Coen}_3]\text{I}_3$	0.9996	-0.045 ₈	-0.003	520.7	-14800	-14830
"	0.9947	-0.045 ₈	-0.003	520.8	-14870	
$[\text{Coen}_3](\text{NO}_3)_3$	0.9913	-0.081	-0.009	520.9	-18100	-18090
"	0.9957	-0.081 ₃	-0.004 ₈	520.8	-18080	

where $-\Delta H_k$, $-\Delta H_A$ and $-\Delta H_{kA}$ are the heats of formation of the gaseous complex cation, gaseous anion, and solid salt, respectively, and U_{kA} is the space-lattice energy of the complex salt. The heats of formation of simple gaseous anions are listed in tables [11]; the heats of formation of polyatomic gaseous anions were computed previously [13]; and the space-lattice energy of a complex salt was always computed from the Kapustinsky equation [14].

To employ the latter equation we must know the radii of the complex ions. The radii of the $[\text{Co}(\text{NH}_3)_6]^{..}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{..}$ ions were found, from the data of the X-ray analysis of the luteo and roseo salts [15, 16] to equal 2.40 Å. We also used this value for the radius of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{..}$. Comparing a number of thermochemical figures for complex salts with those for the ethylene diamine, we established that the thermochemical radii of the $[\text{M en}_3]^{..}$ ions [13] exceeded that for $[\text{M}(\text{NH}_3)_6]^{..}$ by about 0.1 Å. This rule was used by us to evaluate the thermochemical radius of $[\text{Coen}_3]^{..}$.

Using these values of the ion radii and the thermochemical data obtained by us, we computed the heats of formation of the gaseous ions $[\text{Co}(\text{NH}_3)_6]^{..}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{..}$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{..}$ and $[\text{Coen}_3]^{..}$, by applying Equation (I).

TABLE 2
Heat of Solution

Formula of Salt	Weight g	Dilu-tion	Change in tempera-ture in °C corrected for radiation	Radia-tion correc-tion	Heat capacity of the calorimeter, cal.	Heat of solu-tion (Cal.)	Mean value of heat of solution (cal.)
[Co(NH ₃) ₆]Cl ₃	0.6827	10876	-0.043 ₈	+0.002	529.1	-9084	-8970
"	0.6785	10931	-0.042 ₈	-0.001	528.5	-8920	
"	0.6965	10656	-0.043 ₈	-0.004	528.9	-8900	
[Co(NH ₃) ₆]Br ₃	0.6853	16245	-0.040 ₇	+0.003	529.3	-12620	-12760
"	0.6860	16205	-0.041 ₈	+0.002	528.6	-12900	
[Co(NH ₃) ₆](NO ₃) ₃ ..	0.4687	21022	-0.045 ₈	0.000	528.7	-17960	-17890
"	0.4827	19971	-0.046 ₉	0.000	529.3	-17840	
"	0.7018	13731	-0.068 ₃	-0.003	529.1	-17880	
"	0.7083	13602	-0.069	-0.003	529.0	-17890	
[Co(NH ₃) ₅ H ₂ O]Cl ₃ ..	0.9963	74.76	-0.041 ₈	-0.004	528.8	-5960	-5880
"	0.9990	7459	-0.040 ₈	-0.010	529.0	-5800	
[Co(NH ₃) ₅ (H ₂ O)]I ₃ ..	0.6060	24864	-0.026 ₅	-0.002	529.0	-12560	-12590
"	0.6027	25005	-0.028 ₅	-0.001	529.1	-12630	
[Co(NH ₃) ₄ (H ₂ O) ₂]Cl ₃ ..	0.6904	10834	-0.028	+0.005	529.0	-5780	-5800
"	0.6972	10728	-0.028 ₅	0.000	529.0	-5830	
[Coen ₃]I ₃	0.6996	24594	-0.025 ₅	-0.005	529.0	-11950	-11910
"	0.6978	24658	-0.025 ₃	-0.004 ₈	529.0	-11880	
[Coen ₃](NO ₃) ₃	0.6961	16956	0.047	-0.004	529.1	-15190	-15150
"	0.6996	16871	0.047	-0.002	529.1	-15110	

TABLE 3
Heat of Formation

Formula of Salt	Heat of forma-tion computed from heat of reaction (cal.)	Heat of forma-tion computed from heat of solution (cal.)
[Co(NH ₃) ₆]Cl ₃	274.1	274.0
[Co(NH ₃) ₆]Br ₃	244.5	244.8
[Co(NH ₃) ₆]I ₃	201.6	-
[Co(NH ₃) ₆](NO ₃) ₃ ..	311.5	(311.5)
[Co(NH ₃) ₅ H ₂ O]Cl ₃ ..	312.7	313.0
[Co(NH ₃) ₄ (H ₂ O) ₂]Cl ₃ ..	360.6	-
[Co(NH ₃) ₅ H ₂ O]I ₃ ...	240.9	240.8
[Coen ₃]I ₃	133.2	133.2
[Coen ₃](NO ₃) ₃	243.9	(243.9)

The results we obtained are listed in Table 5.

The thermal stability of gaseous complex ions is characterized by the heat of reaction as follows:



where $\text{A}(\text{g})$ is the molecule of the additive in the gaseous state. The heat of formation of the gaseous ion $\text{Co}^{\cdot\cdot\cdot}$ is unknown, which is why we denoted it by X ; the heats of formation of the gaseous additives are known [11,17]; and we computed the heats of formation of the gaseous complex ions. Using these values, we found the heat of reaction (II) for all the ions listed in Table 5.

TABLE 4

Heat of Formation of Ions

Ion formula	Heat of formation (Cal.)	Remarks
$[\text{Co}(\text{NH}_3)_5]^{\cdot\cdot\cdot}\text{aq} \dots\dots\dots$	146.0	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{\cdot\cdot\cdot}\text{aq} \dots\dots\dots$	188.1	
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}\text{aq} \dots$	235.7	
$[\text{Coen}_3]^{\cdot\cdot\cdot}\text{aq} \dots\dots\dots$	81.2	Figures by Lamb and Simmons [1]

TABLE 5

Thermochemical Character of Complex Ions of Cobalt

Ions	Heat of formation in gaseous state (Cal.)	Heat of reaction (II) - Q_1 in Cal.	Heat of reaction III - Q_2 (in Cal.)	Remarks
$[\text{Coen}_3]^{\cdot\cdot\cdot} \dots\dots\dots$	-712	$x - 693$	33.7 - y	
$[\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot} \dots\dots\dots$	-658	$x - 724$	29.9 - y	
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{\cdot\cdot\cdot} \dots\dots$	-619	$x - 732$	23.0 - y	
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot} \dots$	-572	$x - 732$	21.5 - y	The heat of formation of the $\text{Co}^{\cdot\cdot\cdot}$ ion in aqueous solution is denoted by y .

Comparison of the figures obtained indicates that the stability of gaseous complex ions diminishes in the following order: $[\text{Coen}_3]^{\cdot\cdot\cdot} > [\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot} > [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{\cdot\cdot\cdot} > [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}$. Thus, the most stable of the cobalt (III) complex ions are the ethylene diamine complexes, the ammines being less stable, and the aquo salts even less stable.

A comparison of the heats of formation of the complex ions in aqueous solutions of the central hydrated ion and the hydrated additives is likewise of interest, viz., the heat of the reaction:



It should be noted, however, that these heats of reaction provide a comparison characteristic of the thermal stability of complex cations, relating solely to an aqueous solution, since Q_2 is determined not only by the heat of formation

of the complex ion in the gaseous state from the additives and the gaseous central ion, but also by the heat of hydration of the particles participating in Reaction (III).

Denoting by y the unknown value of the heat of formation of $\text{Co}^{\cdot\cdot\cdot}\text{aq}$, we computed the value of Q_2 and list it in Table 5. Comparison of the results obtained indicates that the heat of formation of the complex ions of cobalt (III) in aqueous solutions vary as do the values of Q_1 for gaseous ions, irrespective of the complicating circumstances mentioned above.

Lastly, the material obtained by us enable us to arrive at some conclusions concerning the heats of hydration of complex ions.

The heat of solution of a salt is, as we know, a function of the heats of hydration of the ions and the energies of the space lattice:

$$L = L_k^+ + L_A^- - U_{kA}, \quad (2)$$

where L is the heat of solution of the salt; L_k^+ and L_A^- are the heats of hydration of the cation and anion, respectively; and U_{kA} is the space-lattice energy of the salt.

Since the radii of the ions $[\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{\cdot\cdot\cdot}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}$ are practically identical, the space-lattice energy of salts with the same anion would be the same for all three cases. Hence, the differences in the heats of solution in this case depend on the differences in the heats of hydration of the three cations mentioned above. The heats of solution of the roseo salts (Table 2) are always higher than for the corresponding luteo salts. This circumstance enables us to express the supposition that substituting the H_2O molecule for the NH_3 molecule in the complex ion increases the latter's heat of hydration.

SUMMARY

1. The heats of reaction with a 0.26 molar solution of Na_2S were determined for the following salts: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, $[\text{Co}(\text{NH}_3)_6]\text{I}_3$, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$, $[\text{Coen}_3]\text{I}_3$, and $[\text{Coen}_3](\text{NO}_3)_3$ (Table 1).

2. The heats of solution in water were determined for the following complex cobalt salts: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$, $[\text{Coen}_3]\text{I}_3$ and $[\text{Coen}_3](\text{NO}_3)_3$ (Table 2).

3. With the data obtained as a basis, the heats of formation of the following complex salts have been computed for the solid state: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$, $[\text{Co}(\text{NH}_3)_6]\text{I}_3$, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$, $[\text{Coen}_3]\text{I}_3$ and $[\text{Coen}_3](\text{NO}_3)_3$ (Table 3). The heats of formation of the following complex ions in an aqueous solution have been computed: $[\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot}$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}$, and $[\text{Coen}_3]^{\cdot\cdot\cdot}$, (Table 4).

4. Employing the Kapustinsky equation [14], we have computed the heats of formation of the following gaseous ions: $[\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{\cdot\cdot\cdot}$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{\cdot\cdot\cdot}$ and $[\text{Coen}_3]^{\cdot\cdot\cdot}$ (Table 5).

5. The heats of formation of complex ions consisting of a central ion and additives in the gaseous and dissolved states have been compared. It has been shown that in both cases the thermal stability falls into the following sequence: $[\text{Co en}_3]^{...} > [\text{Co}(\text{NH}_3)_6]^{...} > [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{...} > [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{...}$.

In conclusion, it is our pleasant obligation to express our sincere gratitude to A. F. Kapustinsky for his valuable advice and the attention he has devoted to the present paper.

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THERMOCHEMICAL RELATIONSHIPS IN THE WERNER-MIOLATI SERIES FOR COMPLEX COMPOUNDS OF COBALT (III)

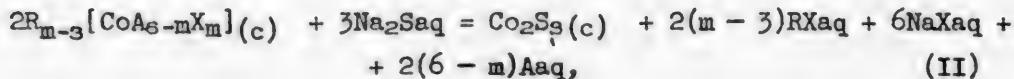
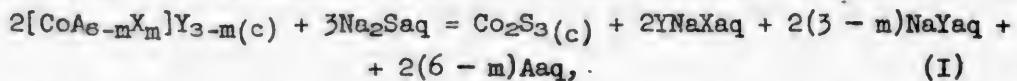
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In previous papers [1,2] we reported the thermochemical data obtained by us for acidopentammine salts of cobalt (III) and for the complex salts of cobalt (III) with neutral additives.

Continuing our systematic investigation of the thermochemistry of the complex compounds of cobalt (III), we resolved to obtain data on the transitional Werner-Miolati series. Series of this sort have been prepared for various groups of complex compounds and their properties studied, but no one, however, has investigated the Werner-Miolati series thermochemically.

The chosen subject of our investigation was the series: $[Co(NH_3)_6]X_3$, $[Co(NH_3)_5 \cdot NO_2]X_2$, $[Co(NH_3)_4(NO_2)_2]X$, $[Co(NH_3)_3(NO_2)_3]$, $R[Co(NH_3)_2(NO_2)_4]$, and $R_3[Co(NO_2)_6]$. Compounds of the $R_2[Co(NH_3)(NO_2)_5]$ type have not been described in the literature. In addition to the compounds listed above, we investigated the compounds of the $[Coen_2(NO_2)_2]X$, $R_3[Co(C_2O_4)_3]$ type, as well as several others. To calculate the heat of formation of the compounds listed, we measured the heat of reaction for the listed crystalline compounds with a 0.26 molar solution of Na_2S , proceeding according to the following equations:



where A is the neutral additive, X and Y are single-charge anions, and R is a single-charge cation. The apparatus and the methods used in the determinations are the same as for the acidopentammine salts of cobalt (I).

All measurements were effected at 25°.

EXPERIMENTAL

The dinitrotetrammine salts of cobalt (cis and trans isomers) were prepared by the method described by Jorgensen [3]. The following compounds were likewise prepared according to Jorgensen [4,5,6,7]: $[Co(NH_3)_3(NO_2)_3]$, $K[Co(NH_3)_2(NO_2)_4]$, $NH_4[Co(NH_3)_2(NO_2)_4]$, $NH_4[Co(NH_3)_2(NO_2)_2C_2O_4]$,

$K[Co(NH_3)_2(NO_2)_2C_2O_4]$, $Na[Co(NH_3)_2(NO_2)_2C_2O_4]$, $[Co(NH_3)_6][Co(NO_2)_6]$, $[Co(NH_3)_5NO_2]_3$, $[Co(NO_2)_6]_2$ and $[Coen_2Cl_2]Cl$.

The hexanitritocobaltammine of sodium was prepared by the Biilman method [8]; $[Co(NH_3)_6](NO_2)_6$ according to Reisenfeld, $[Coen_2(NO_2)_2]X$ salts were prepared according to Werner and Humphrey [10]; $[Co(NH_3)_4(H_2O) \cdot NO_3](NO_3)_2$ was prepared by the Wortmann method [12]; $[Co(NH_3)_6][Co(C_2O_4)_3] \cdot 3H_2O$ was prepared by the Pfeiffer-Basci method [13]; and $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ was prepared by the Sorensen method [14]. The *cis* $[Co(NH_3)_4(NO_2)_2]I$ was prepared by us by mixing a solution of $[Co(NH_3)_4(NO_2)_2]Cl$ with a concentrated solution of KI. Analysis of the precipitate formed indicated that the salt contained 36.48% of iodine (theoretically 36.68%).

When the roseochloride solution was mixed with the solution of $Na_2[Co(NO_2)_6]$, $[Co(NH_3)_5H_2O][Co(NO_2)_6]$ was precipitated. The precipitate was filtered out, washed with water, and air dried. The salt prepared contained 23.61% of cobalt (theoretical value = 23.71%).

We determined the heats of reaction with a 0.26 molar solution of Na_2S for the following compounds: $[Co(NH_3)_4(NO_2)_2]Cl$ (cis and trans isomers), $[Co(NH_3)_4 \cdot (NO_2)_2]NO_3$ (cis and trans isomers), $[Co(NH_3)_4(NO_2)_2]I$ (cis and trans isomers), $[Co(NH_3)_3(NO_2)]_3$, $NH_4[Co(NH_3)_2(NO_2)_4]$, $K[Co(NH_3)_2(NO_2)_4]$, $Na_3[Co(NO_2)_6]$, $[Co(NH_3)_6][Co(NO_2)_6]$, $[Co(NH_3)_5H_2O][Co(NO_2)_6]$, $[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$, $[Coen_2(NO_2)_2]NO_3$ (cis isomer), $[CoenNH_3(NO_2)_3]$, $NH_4[Co(NH_3)_2(NO_2)_2C_2O_4]$, $K[Co(NH_3)_2(NO_2)_2C_2O_4]$, $Na[Co(NH_3)_2(NO_2)_2C_2O_4]$, $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, $[Co \cdot (NH_3)_6][Co(C_2O_4)_3] \cdot 3H_2O$, $[Co(NH_3)_4(H_2O)NO_3](NO_3)_2$ and trans- $[Coen_2Cl_2]NO_3$. The results obtained are listed in Table 1.

The heat of solution in water was determined solely for the conspicuously soluble salts, namely: $[Co(NH_3)_4(NO_2)_2]Cl$ (cis and trans isomers), $[Co(NH_3)_4 \cdot (NO_2)_2]NO_3$ (cis and trans isomers), $NH_4[Co(NH_3)_2(NO_2)_4]$, $K[Co(NH_3)_2(NO_2)_4]$, $Na_3[Co(NO_2)_6]$, cis- $[Coen_2(NO_2)_2]NO_3$, $NH_4[Co(NH_3)_2(NO_2)_2C_2O_4]$, $K[Co \cdot (NH_3)_2(NO_2)_2C_2O_4]$, $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, trans- $[Coen_2Cl_2]NO_3$ and $[Co \cdot (NH_3)_4(H_2O)NO_3](NO_3)_2$.

Owing to the extremely low solubility of $[Co(NH_3)_3(NO_2)_3]$, the heats of solution obtained by us in this case must be looked upon as quite approximate. The results of the measurements made and the list of the values of the heats of solution obtained are listed in Table 2.

From the values of the heats of reaction of the crystalline complex compounds with a 0.26 molar solution of Na_2S we computed their heats of formation under standard conditions (25°). The heats of formation of all the substances entering into Reactions (I) and (II) are taken from Bichowsky's and Rossini's Thermochemistry [15]. The heats of formation of all the complex compounds for which the heats of reaction with a 0.26 molar solution of Na_2S were determined are listed in Table 3.

The heats of formation in aqueous solution of the following complex ions were computed from the values of the heats of formation of the crystalline complex salts of cobalt (III) obtained by us: $[Co(NH_3)_4 \cdot (NO_2)_2]'$ (cis and trans isomers), $[Co(NH_3)_2(NO_2)_4]''$, $[Co(NO_2)_6]'''$, $[Coen_2(NO_2)_2]'$, $[Co(NH_3)_2(NO_2)_2C_2O_4]'$, $[Co(C_2O_4)_3]'''$, and $[Co(NH_3)_4(H_2O)NO_3]'''$. In all computations, the heats of formation of NO_3^- , NH_4^+ , Na^+ , K^+ and Cl^- ions in aqueous solution are taken from Thermochemistry by Bichowsky and Rossini [15]. The values of the

Table 1

Heat of Reaction of Crystalline Complex Compounds of Cobalt (III) with a 0.2M Molar Solution of Na₂S at 25°

Formula	Heat of reaction (cal)	Initial temperature (°C)	Normal reading (cal)	Heat of reaction (cal)	Mean value of heat of reac- tion (cal)
trans-[Co(NH ₃) ₄ (NO ₂) ₂] Cl	-0.655	-0.051	+0.01	520.7	-7510
cis-[Co(NH ₃) ₄ (NO ₂) ₂] Cl	0.939	-0.056	+0.02	520.7	-7520
cis-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	0.703	-0.134	0.00	520.7	-6300
trans-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	0.917	-0.023	+0.001	520.3	-7720
cis-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	-1.933	-0.010	+0.001	521.2	-8840
cis-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	0.597	-0.010	+0.003	520.7	-8410
trans-[Co(NH ₃) ₄ (N ⁺) ₂] Cl	0.926	-0.013	+0.001	520.5	-7760
cis-[Co(NH ₃) ₄ (N ⁺) ₂] Cl	0.973	-0.042	0.00	520.9	-7750
cis-[Co(NH ₃) ₄ (N ⁺) ₂] Cl	0.691	-0.033	+0.003	521.2	-8740
[Co(NH ₃) ₄ (NO ₂) ₂] ₂	0.697	-0.032	0.000	521.0	-8580
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	0.612	-0.002	0.000	520.9	+380
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	0.657	+0.002	+0.003	520.7	+380
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	1.013	-0.002	-0.002	520.9	-307
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	1.013	-0.003	-0.007	520.9	-380
K[Co(NH ₃) ₄ (NO ₂) ₂]	0.945	-0.015	-0.002	520.8	-2480
K[Co(NH ₃) ₄ (NO ₂) ₂]	0.956	-0.015	-0.002	521.1	-2450
Na ₂ [Co(NH ₃) ₄] ₂	1.000	+0.059	-0.029	520.7	+12560
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.9225	+0.002	+0.002	520.8	+13540
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.9465	+0.005	+0.009	520.7	+13510
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.9567	+0.002	+0.002	521.0	+13500
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.9515	+0.073	-0.023	520.9	+19600
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.9500	+0.074	-0.020	520.8	+19550
[Co(NH ₃) ₄][CO(NO ₂) ₂]	1.0000	+0.032	-0.020	520.8	+24620
[Co(NH ₃) ₄][CO(NO ₂) ₂]	0.7000	+0.032	-0.015	520.8	+24620
cis-[Coen ₂ (NO ₂) ₂] NO ₂	0.785	-0.038	-0.003	521.0	-8520
cis-[Coen ₂ (NO ₂) ₂] NO ₂	0.9445	-0.060	-0.015	520.9	-8800
[Coen ₂ (NH ₃) ₂][NO ₂] ₂	0.7274	-0.011	-0.003	520.9	-2800
[Coen ₂ (NH ₃) ₂][NO ₂] ₂	0.7910	-0.013	-0.004	520.8	-2350
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	0.975	+0.061	-0.017	520.7	+9270
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	0.9990	+0.061	-0.017	520.9	+9270
K[Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	1.0002	+0.056	-0.011	521.0	+9110
K[Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	1.0005	+0.056	-0.010	520.9	+9110
Na ₂ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	1.0016	+0.009	-0.018	520.8	+13960
Na ₂ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	1.0031	+0.007	-0.019	520.8	+13940
Na ₂ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄	1.0035	+0.008	-0.009	520.7	+13640
K ₂ [Co(C ₂ O ₄) ₂] · 3H ₂ O	1.0000	+0.109	-0.010	520.9	+28160
[Co(NH ₃) ₄][Co(C ₂ O ₄) ₂] · 3H ₂ O	0.9795	+0.132	-0.020	520.9	+35180
[Co(NH ₃) ₄][Co(C ₂ O ₄) ₂] · 3H ₂ O	0.9794	+0.127	-0.015	520.9	+35260
[Co(NH ₃) ₄ (H ₂ O) NO ₂] (NO ₂)	1.0000	+0.028	-0.002	520.9	+4920
[Co(NH ₃) ₄ (H ₂ O) NO ₂] (NO ₂)	0.9567	+0.028	-0.008	520.9	+4940
trans-[Coen ₂ Cl ₂] NO ₂	0.9728	+0.035	-0.002	520.9	+6130
trans-[Coen ₂ Cl ₂] NO ₂	0.9645	+0.037	-0.009	520.9	+6140

Table 2

Heat of Solution of Crystalline Complex Compounds of Cobalt (III) in Water at 25°

Compound formula	Weight quantity (g)	Calorimeter efficiency (%)	Heat of solution (cal)	Heat of correction (cal)	Thermal capacity of calorimeter (cal/°C)	Heat of reac- tion (cal)
trans-[Co(NH ₃) ₄ (NO ₂) ₂] Cl	0.4940	1427	-0.038	0.000	528.9	-10550
.....	0.6933	10190	-0.054	-0.054	529.4	-10490
.....	0.6933	10154	-0.054	+0.004	528.7	-10450
cis-[Co(NH ₃) ₄ (NO ₂) ₂] Cl	0.6949	10170	-0.048	+0.001	529.2	-9480
.....	0.6978	10123	-0.048	+0.001	529.2	-9460
trans-Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	0.4922	15840	-0.039	+0.002	529.5	-12000
.....	0.4932	15627	-0.039	+0.004	529.0	-11840
cis-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂	0.5944	7845	-0.081	+0.002	529.0	-12190
.....	0.5997	7805	-0.081	+0.004	529.1	-12130
trans-[Co(NH ₃) ₄ (NO ₂) ₂] I	0.4967	19342	-0.032	+0.002	529.2	-12020
.....	0.4902	19553	-0.032	+0.007	528.8	-12170
[Co(NH ₃) ₄ (NO ₂) ₂] I	0.2975	23146	-0.019	+0.011	529.1	-8540
.....	0.2945	23055	-0.022	+0.017	528.8	-8450
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	0.7031	11645	-0.049	-0.006	528.9	-10880
NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]	0.7012	11677	-0.049	-0.011	528.9	-10910
K[Co(NH ₃) ₄ (NO ₂) ₂]	0.2980	23431	-0.028	+0.006	528.8	-13300
.....	0.3010	29132	-0.028	+0.004	528.7	-13340
Na ₂ [Co(NO ₂) ₂]	1.0000	11212	-0.081	-0.008	529.0	-17420
.....	0.6945	16052	-0.057	-0.007	529.0	-17440
cis-[Coen ₂ (NO ₂) ₂] NO ₂	0.6935	13285	-0.040	-0.012	529.0	-10330
.....	0.6977	13248	-0.040	-0.006	528.9	-10300
NH ₄ [Co(NH ₃) ₂ (NO ₂) ₂ C ₂ O ₄]	0.6043	13367	-0.037	-0.004	529.0	-9610
.....	0.6016	13441	-0.037	-0.003	529.0	-9660
K[Co(NH ₃) ₂ (NO ₂) ₂ C ₂ O ₄]	0.5010	17236	-0.029	-0.005	529.0	-9700
.....	0.5022	17257	-0.029	-0.005	529.1	-9700
K ₂ [Co(C ₂ O ₄) ₂] · 3H ₂ O	0.7040	19495	-0.041	-0.001	529.0	-17830
.....	0.7031	19499	-0.048	-0.001	528.9	-17840
trans-[Coen ₂ Cl ₂] NO ₂	0.4934	17375	-0.031	-0.001	529.0	-10470
.....	0.6934	12400	-0.048	-0.003	529.0	-10550
[Co(NH ₃) ₂ (H ₂ O) NO ₂] (NO ₂)	0.6960	13167	-0.050	-0.001	529.1	-12650
.....	0.7011	13109	-0.050	-0.001	529.1	-12690

Table 4

Heat of Formation of Complex Ions in Aqueous Solution Under Standard Conditions

Ion	Heat of formation (cal)	Formula of initial complex salt			
trans-[Co(NH ₃) ₄ (NO ₂) ₂] · ag	159.14	trans-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂			
cis-[Co(NH ₃) ₄ (NO ₂) ₂] · ag	159.89	cis-[Co(NH ₃) ₄ (NO ₂) ₂] NO ₂			
[Co(NH ₃) ₄ (NO ₂) ₂] · ag	164.93	NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂]			
[Co(NH ₃) ₄ (NO ₂) ₂] · ag	157.94	Na ₂ [Co(NH ₃) ₄ (NO ₂) ₂]			
cis-[Coen ₂ (NO ₂) ₂] · ag	113.26	cis-[Coen ₂ (NO ₂) ₂] NO ₂			
[Co(NH ₃) ₄ (NO ₂) ₂] · C ₂ O ₄ · ag	301.13	NH ₄ [Co(NH ₃) ₄ (NO ₂) ₂] C ₂ O ₄			
[Co(NH ₃) ₄ (NO ₂) ₂] · ag	535.76	K ₂ [Co(C ₂ O ₄) ₂] · 3H ₂ O			
[Co(NH ₃) ₄ (H ₂ O) NO ₂] · ag	212.09	[Co(NH ₃) ₄ (H ₂ O) NO ₂] (NO ₂)			
[Co(NH ₃) ₄ (H ₂ O) NO ₂] · ag	126.44	[Coen ₂ Cl ₂] Cl · M ⁺			
Ion	Radius of ion (Å)	Heat of formation of aqueou- sion (cal)	Heat of reaction (III) Q ₁ (in Cal)	Heat of reaction (IV) Q ₂ (in Cal)	Liter- ature sources
[Co(NH ₃) ₄] ⁺	2.40	-658	x-724	29.9-y	■
[Co(NH ₃) ₄ NO ₂] ⁺	2.30	-267	x-355	31.1-y	■
cis-[Co(NH ₃) ₄ NO ₂] ⁺	(2.37)	(15)	(x-92)	31.3-y	■
trans-[Co(NH ₃) ₄ NO ₂] ⁺	(2.37)	(22)	x+69	23.0-y	■
[Co(NH ₃) ₄] ²⁺	2.20	-2220	x+266	6.1-y	■
[Co(NH ₃) ₄] ²⁺	2.39	-4	x-374	19.7-y	■
cis-[Co(NH ₃) ₄] ²⁺	2.36	-257	x-374	8.2-y	■
trans-[Co(NH ₃) ₄] ²⁺	2.37	-	-	9-y	■
[Coen ₂] ⁺	2.5	-712	x-693	33.7-y	■
cis-[Coen ₂] ⁺	-	-	-	33.7-y	■
cis-[Coen ₂] ⁺	-	-	-	16.7-y	■
trans-[Coen ₂] ⁺	-	-	-	15.5-y	■
[Co(NH ₃) ₄ (H ₂ O)NO ₂] ²⁻	2.40	-202	x-358	17.1-y	■
[Co(NH ₃) ₄ (H ₂ O) ₂ CO ₃] ²⁻	-	-	-	16.2-y	■
[Co(NH ₃) ₄] ³⁻	2.43	-263	x-377	21.1-y	■
[Co(NH ₃) ₄] ³⁻	-	-	-	11.0-y	■
[Co(NH ₃) ₄ NO] ²⁻	-	-	-	11.4-y	■
[Co(NH ₃) ₄ NO] ²⁻	2.40	-241	x-378	27.9-y	■
[Co(NH ₃) ₄ CO] ²⁻	-	-	-	20.9-y	■

The heat of formation of the gaseous ion Co⁺⁺ is denoted by x, and the heat of formation of the Co⁺⁺ in aqueous solution is denoted by y.

heat of formation of the ions in aqueous solution obtained by us are listed in Table 4.

The heats of formation for a number of complex salts can be computed not only from the heat of reaction with a 0.26 molar solution of Na_2S , but also from their heats of solution in water, employing the above-mentioned values of the heats of formation of the ions in aqueous solution.

The heats of formation of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ (cis and trans isomers), trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{I}$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$ and trans- $[\text{Coen}_2\text{Cl}_2]\text{NO}_3$ were computed in this manner.

Evaluation of Results

In our previous paper [2] we pointed out that judging the stability of complex ions requires a comparison of their stability in the gaseous state, as in this case the influence of external ions is excluded.

The heat of formation of gaseous complex ions could be computed only when data were available that permitted the calculation of the space-lattice energy of the complex salt [18]. The radius of the complex ions must be known before the Kapustinsky equation [17] can be applied in this case.

The methods of computing the radii of ions from thermochemical data were proposed by Kapustinsky [18] and one of the present authors [19]. Applying the method of differences between the heats of formation of solid salts [19] with the same ion, we computed the thermochemical radii of the $[\text{Co}(\text{NO}_2)_6]^{1-}$ (from its heats of formation), $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}][\text{Co}(\text{NO}_2)_6]$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2\cdot[\text{Co}(\text{NO}_2)_6]]_2$ and $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^{1-}$ ion (from the heats of formation of its potassium and ammonium salts).

The thermochemical radii of both ions were found to equal 2.50 Å. From these figures and the values of the radii of the $[\text{Co}(\text{NH}_3)_6]^{1-}$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{1-}$ ions, the appraisable value for the radius of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{1-}$ was taken as 2.4 Å. Evidently, in the croceo- and flavo-salts ionic dipole forces act between the ions in addition to the forces of the electro-static attraction of the ions, and thus in this case the "method of differences" does not yield the desired results.

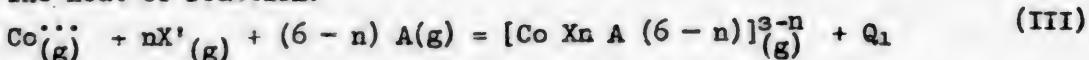
It was previously found [2] that the radii of the $[\text{Co}(\text{NH}_3)_6]^{1-}$ and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{1-}$ ions are alike; this circumstance permits us to assume that the radii of the $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{1-}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{NO}_3)]^{1-}$ ions will also not be far apart, and, hence, the radius of the latter ion may be taken to equal 2.40 Å.

The heats of formation of gaseous complex ions were computed from the following equation:

$$-\Delta H_k = \Delta H_A - \Delta H_{kA} - U_{kA}, \quad (I)$$

where $-\Delta H_k$, $-\Delta H_A$ and $-\Delta H_{kA}$ are the heats of formation of the gaseous ions and the solid salt, respectively, and U_{kA} is the lattice energy of the complex salt, as computed from the Kapustinsky equation [17]. The values of the heats of formation of gaseous complex ions thus obtained are listed in the third column of Table 5.

The heat of reaction:

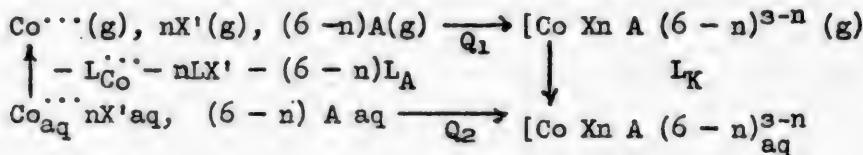


is listed in the fourth column of Table 5. The unknown value of the heat of formation of the gaseous ion $\text{Co}^{\cdot\cdot\cdot}$ is denoted by X .

It follows from the data listed in Table 5 that the replacement of the NH_3 molecule in the gaseous cation $[\text{Co}(\text{NH}_3)_6]^{\cdot\cdot\cdot}$ by the NO_2^- , Cl' , and NO_3^- anion is accompanied by the liberation of considerable heat. It follows from the data previously published by us [1,2] that the same sort of phenomenon takes place with the other anions investigated by us (Br' and I'). The replacement of another NH_3 molecule by a NO_2^- anion (in the gaseous cation $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2-}$) is likewise accompanied by the liberation of heat, though in this latter case the quantity of heat liberated is somewhat smaller. The further replacement of NH_3 molecules by gaseous NO_3^- anions is accompanied by a smaller thermal effect, and, finally, the replacement of two NH_3 molecules by NO_3^- anions in the gaseous $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^{2-}$ anion is accompanied by a negative thermal effect. Thus, in the gaseous state the complex ions that are in the center of the Werner-Miolati series exhibit the greatest thermal stability.

The heat of formation of the complex ion from hydrated additives and the central ion in an aqueous solution depends not only on its thermal stability in the gaseous state, but also upon a number of complicating factors involving the different values of the energy of hydration of the particles entering into the reaction.

Let us consider the following thermochemical cycle as evidence of this assertion:



Whence:

$$Q_2 = Q_1 + L_K - L_{\text{Co}}^{\cdot\cdot\cdot} - nL_{X'} - (6-n)L_A. \quad (2)$$

It follows from this equation that the heat of formation of a complex ion in a solution (Q_2) is determined by its heat of formation in the gaseous state (Q_1) and the heats of hydration of the complex ion (L_K), the additives ($L_{X'}$ and L_A), and the central ion ($L_{\text{Co}}^{\cdot\cdot\cdot}$). In the case of complex ions with the same central ion, the differences in Q_2 depend upon the differences in Q_1 , the differences in the heats of hydration of the complex ions, and lastly, the differences in the heats of hydration of the additives. Since the heat of hydration of a complex ion depends chiefly upon its charge, the heat of formation of a complex ion with a large charge will be larger than the heat of formation of a complex ion with a small charge, all other conditions being equal.

On the basis of these relationships it is possible, at least qualitatively, to explain the essentially different order of changes in the heats of formation of complex ions in solutions in the Werner-Miolati series compared to the order of changes of their heat of formation in the gaseous state. Designating the unknown heat of formation of the $\text{Co}^{\cdot\cdot\cdot}$ ion in an aqueous solution by Y , we computed the heat of formation for a series of ions:



The values of Q_2 obtained by us are listed in the fifth column of Table 5. The replacement of NH_3 molecules by Cl' , NO_3' , Br' , CO_3'' and SO_4'' anions and molecules of H_2O in an aqueous solution is accompanied by a negative thermal effect. The NO_2' anion and the molecule of ethylene diamine, which liberate heat when they replace the NH_3 molecule, are the exceptions to this rule. Moreover, in the case of NO_2' anions, the $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$ - anion is found the most stable; further replacement of NH_3 molecules by NO_2' is accompanied by a negative thermal effect. Hence, the most stable, thermally, of the $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]_{\text{aq}}^{3-n}$ series in aqueous solution are found to be the middle members of the series, and not the end members. In the $[\text{Co}(\text{NH}_3)_{6-n}\text{Cl}_n]_{\text{aq}}^{3-n}$ series the heat of formation of the complex ion (Q_2) drops as the chlorine anions accumulate.

Our determinations have resulted in a considerable increase in the available material on the thermochemistry of the geometrical isomers of complex compounds. Thermochemical data have been obtained for the croceo- and flavo-salts to supplement the studies already made of the praseo- and purpureo-salts [20]. The heats of formation of the cis and trans salts differ but little; we were unable to find any regularity in this variation as yet.

In our preceding paper we pointed out that the replacement of NH_3 molecules by molecules of H_2O results in an increase in the ion's heat of hydration and, hence, an increase in the heat of solution of the corresponding salts. Here, in corroboration of that rule we may cite still another example: the heat of solution of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}_3](\text{NO}_3)_2$ is higher than the heat of formation of $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$ (- 12.67 vs. - 14.8 Cal).

SUMMARY

1. The heat of reaction with a 0.26 molar solution of Na_2S was determined for the following crystalline compounds: $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ (cis and trans isomers), $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2](\text{NO}_3)$ (cis and trans isomers), $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{I}$ (cis and trans isomers), $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}][\text{Co}(\text{NO}_2)_6]$, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]_3[\text{Co}(\text{NO}_2)_6]_2$, $[\text{Coen}_2(\text{NO}_2)_2]\text{NO}_3$ (cis isomer), $[\text{Coen} \text{NH}_3(\text{NO}_2)_3]$, $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$, $\text{Na}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$, $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}_3](\text{NO}_3)_2$ and $[\text{Coen}_2\text{Cl}_2]\text{NO}_3$ (trans isomer) (Table 1).

2. The heat of solution in water has been measured for the following crystalline complex compounds of cobalt (III): $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ (cis and trans isomers), $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$ (cis and trans isomers), trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{I}$, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$, cis $[\text{Coen}_2(\text{NO}_2)_2]\text{NO}_3$, $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]$, $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, trans $[\text{Coen}_2\text{Cl}_2]\text{NO}_3$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}_3](\text{NO}_3)_2$ (Table 2).

3. The heat of formation under standard conditions was computed for all the salts listed in Par. 1 (Table 3).

4. The heat of formation in aqueous solution under standard conditions was computed for the following complex ions: $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ (cis and trans isomers), $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^+$, $[\text{Co}(\text{NO}_2)_6]^{3-}$, cis $[\text{Coen}_2(\text{NO}_2)_2]$, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]^+$, $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}_3]^{2-}$ (Table 4)

5. The heat of formation was computed for the following gaseous ions: $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]'$, $[\text{Co}(\text{NO}_2)_6]'''$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{NO}_3]''$ (Table 5).

6. It has been demonstrated that in the series of $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]^{3-n}$ gaseous ions the highest thermal stability is possessed by one of the central members of the series ($[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]'$).

7. The factors affecting the heat of formation of a complex ion in aqueous solution, consisting of hydrated additives and the central ion (Q_2), were explored. It has been shown that in the series of $[\text{Co}(\text{NH}_3)_{6-n}(\text{NO}_2)_n]^{3-n}$ ions in aqueous solutions, Q_2 has the largest value for $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]$. In the $[\text{Co}(\text{NH}_3)_{6-n}Cl_n]^{3-n}$ series Q_2 diminishes as the number of chlorine ions ($n = 1.2$) increases.

In conclusion, we welcome the opportunity of expressing our sincere thanks to A.F.Kapustinsky for the attention he has devoted to the present paper.

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¹ See English translation of CB, p. 569

RESEARCHES IN FORMIC-ACID SYSTEMS. IV

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The present paper submits experimental data on the determination of the molecular weight of the following systems: formic acid - acetone, formic acid - methyl ethyl ketone, and formic acid - methyl propyl ketone.

Table 1

Serial No.	Substance	Temperature		Pressure (mm)
		Melting point	Boiling point	
1	Formic acid	8.3°	-	-
2	Acetone.....	-	55.5°	729
3	Methyl ethyl ketone	-	77.3	729
4	Methyl propyl ketone	-	99.8	728
5	Benzene.....	5.5	-	-

The molecular weight was determined, the diagrams plotted, and the molecular weight computed exactly as in our previous papers [1,2]. Benzene was used as the solvent. After purification the initial substances possessed the constant exhibited in Table 1.

FORMIC ACID - ACETONE SYSTEM

The results of the experimental determination of the molecular weight of the formic acid - acetone system are shown in Table 2. The values of the molecular weight of the solutes, found graphically for concentrations of 0.0, 0.5, 1.0, and 1.5 moles per 1000 g of benzene, are shown in the corresponding isoconcentrate lines of Fig. 1.

The isoconcentrate lines I and II of Fig. 1, concave downward toward the composition axis, as well as the isoconcentrate lines III and IV, all pass through maxima at about 90 mol.% of formic acid. When the constituents are mixed, marked heating is observed.

FORMIC ACID - METHYL ETHYL KETONE SYSTEM

The results of the experimental determination of the molecular weight of

Table 2
Formic Acid - Acetone

HCOOH (mol.%)	Moles of substance in 1000 g of benzene	Δt°	M	HCOOH (mol.%)	Moles of substance in 1000 g of benzene	Δt°	M
100.00	0.1020	0.279	85.6	42.25	0.1178	0.433	73.3
	0.2758	0.701	91.7		0.3906	1.231	84.4
	0.4339	1.055	95.4		0.7051	2.053	90.2
	0.6969	1.592	100.6		1.0792	2.884	97.0
	0.9581	2.074	105.4		1.3823	3.501	101.4
	1.4112	2.784	114.4		31.91	0.819	74.7
90.79	0.1711	0.455	88.7	23.53	0.4096	1.429	77.8
	0.4633	1.125	96.2		0.6235	2.086	80.3
	0.7550	1.699	102.8		0.8475	2.673	84.4
	1.0644	2.249	108.6		1.2014	3.373	88.2
	1.5423	2.970	117.8		0.6664	0.667	69.8
84.18	0.6111	1.464	100.1	11.73	0.4096	1.429	74.5
	1.0000	2.163	107.1		0.5470	1.937	77.5
	1.3164	2.723	113.7		0.7907	2.709	79.1
	1.7121	3.183	125.6		1.0666	3.474	82.2
72.97	0.2570	0.744	86.9	0.00	0.2090	0.903	66.2
	0.5137	1.343	94.5		0.4196	1.722	68.8
	0.7004	1.740	98.8		0.5797	2.317	70.9
	1.0136	2.297	107.4		0.7690	2.972	71.7
62.66	0.2590	0.782	84.6	0.00	1.0705	4.010	72.7
	0.5224	1.445	92.0		0.1582	0.751	61.9
	0.7862	2.019	97.6		0.2519	1.634	62.4
	1.1453	2.717	104.5		0.5348	2.441	62.7
	1.6280	3.500	113.9		0.7507	3.295	64.3
52.33	0.1877	0.594	83.9	0.00	0.9996	4.288	64.8
	0.4299	1.262	88.5				
	0.6812	1.876	93.5				
	1.0332	2.674	98.2				
	1.4211	3.394	105.2				

the formic acid-methyl ethyl ketone system are given in Table 3. The diagram of the molecular weight of this system, plotted with the graphically found values of the molecular weight, is reproduced in Fig. 2. All the isoconcentrate lines of the formic acid - methyl ethyl ketone system (Fig. 2) pass through maxima that are shifted toward the formic-acid end of the system.

Mixing of the components results in marked heating.

FORMIC ACID - METHYL PROPYL KETONE SYSTEM

The results of the experimental determination of the molecular weight of

the formic acid - methyl propyl ketone system are listed in Table 4. the diagram of the molecular weight of this system, plotted with the graphically found values of the molecular weight, is reproduced in Fig. 3. All the isoconcentrate lines (Fig. 3) pass through maxima that are shifted toward the formic-acid end of the system. The preparation of a mixture of formic acid and methyl propyl ketone results in marked heating.

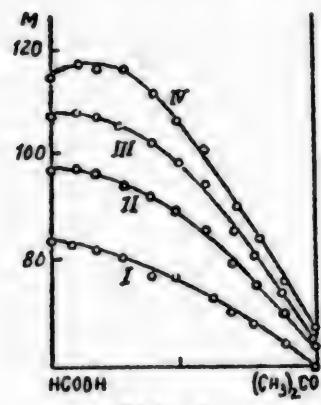


Fig. 1

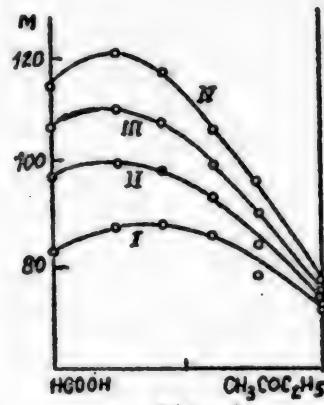


Fig. 2

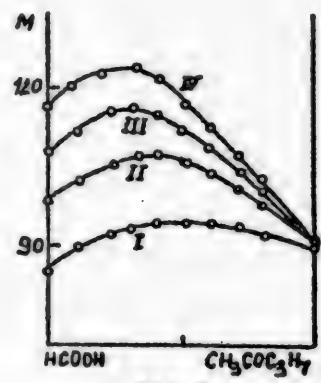


Fig. 3

Table 3
Formic Acid - Methyl Ethyl Ketone

HCOOH (mol. %)	Moles of substance in 1000 g of benzene	Δt°	M	HCOOH (Mol. %)	moles of substance in 1000 g of benzene	Δt°	M
100.00	0.1020	0.279	85.6	40.48	0.2251	0.788	88.9
	0.2758	0.701	91.7		0.4189	1.408	91.7
	0.4339	1.055	95.4		0.8460	2.613	97.9
	0.6969	1.592	100.6		1.1127	3.298	100.9
	0.9581	2.074	105.4		0.1368	0.578	79.4
	1.4112	2.784	114.4		0.3491	1.404	82.3
76.54	0.2523	0.710	93.8	22.95	0.5512	2.132	84.6
	0.4723	1.237	99.3		0.7233	2.688	87.3
	0.7233	1.771	105.3		1.0215	3.620	90.2
	1.0290	2.369	111.0		0.1168	0.585	73.0
	1.2791	2.796	116.1		0.3606	1.758	73.6
59.17	0.1907	0.608	90.1	0.00	0.5014	2.414	73.8
	0.3945	1.171	95.9		0.6809	3.199	74.7
	0.6153	1.710	101.6		0.8121	3.798	74.3
	0.8269	2.203	105.2				
	1.1056	2.801	109.6				
	1.3592	3.282	114.1				

In the series of papers entitled The Viscosity of the Ketones - Organic Acid Systems [3,4,5,6] the chemical interaction of formic acid with acetone, methyl ethyl ketone, and methyl propyl ketone was recorded. The data on the

Table 4

Formic Acid - Methyl Propyl Ketone

HCOOH (mol.%)	moles of substance in 1000 g of benzene	Δt°	M	HCOOH (mol.%)	moles of substance in 1000 g of benzene	Δt°	M
100.00	0.1020	0.279	85.6	49.03	0.1599	0.551	97.9
	0.2758	0.701	91.7		0.3100	1.021	101.7
	0.4339	1.055	95.4		0.4533	1.443	104.5
	0.6969	1.592	100.6		0.6325	1.961	106.4
	0.9581	2.074	105.4		0.8847	2.624	110.1
	1.4112	2.784	114.4		39.77	0.1809	0.668
89.45	0.2875	0.756	96.7	30.06	0.3484	1.219	100.7
	0.5913	1.433	103.8		0.5334	1.803	103.3
	0.9453	2.094	110.1		0.7367	2.417	105.4
	1.1959	2.571	115.9		0.9650	3.048	108.4
79.24	0.2455	0.693	97.5	19.86	0.1623	0.645	94.5
	0.4897	1.280	104.3		0.3191	1.204	98.6
	0.7637	1.862	110.9		0.4932	1.806	100.7
	1.0247	2.386	115.1		0.6444	2.325	101.3
	1.2838	2.842	120.2		0.7982	2.827	102.4
70.25	0.2169	0.657	97.0	0.00	0.9770	3.377	104.0
	0.4457	1.227	105.7		0.1528	0.648	93.4
	0.6570	1.714	110.7		0.3680	1.488	96.7
	0.8831	2.222	113.9		0.5565	2.202	97.7
59.65	0.1835	0.579	100.0	0.00	0.7487	2.908	98.4
	0.3895	1.167	104.4		0.9756	3.685	100.0
	0.6092	1.730	109.2		0.1238	0.614	88.0
	0.8360	2.297	111.8		0.2517	1.221	89.2
	1.1529	2.948	117.0		0.3773	1.813	89.2
					0.5009	2.385	89.2
					0.6405	3.026	89.9
					0.7939	3.700	89.2

molecular weight of the formic acid - acetone, formic acid - methyl ethyl ketone, and formic acid - methyl propyl ketone systems cited here enable us to confirm, without any doubt, the existence of interaction between the components, exhibited in the molecular-weight diagrams in the shape of a maximum (Figs. 1, 2, and 3). As the proportion of the mixture in the benzene increases, the maxima of the curves are shifted toward the formic-acid end; evidently, the interaction of formic acid with the ketones results in the formation of compounds whose composition grows more complex as the concentration of the acid is increased.

SUMMARY

1. The molecular weights of the systems: formic acid - acetone, formic acid - methyl ethyl ketone, and formic acid - methyl propyl ketone, were investigated.

2. The results of the measurement of molecular weight, in agreement with viscosity data, indicate the existence of chemical interaction in the formic acid - acetone, formic acid - methyl ethyl ketone, and formic acid - methyl propyl ketone systems.

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THE INFLUENCE OF ARGININE UPON METHANOL SOLUTIONS OF NaI-KI.

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Little is known regarding the analytical investigation of salt equilibria in nonaqueous systems. The rare research in this field far from satisfies the interest in the problems of solubility and crystallization in nonaqueous solvents.

In nonaqueous solutions of salts, the equilibrium of the system is governed not only by the ionic equilibrium, but by a number of other factors as well. In some nonaqueous systems ionization of the salts is quite impossible; solvates and complexes are formed. Under these conditions equilibrium cannot be determined by the ion product in concentrated non-aqueous systems.

In studying the problems of solution and crystallization in nonaqueous solutions, the relationships among the compositions of the initial system, the solid phase, and the liquid phase are of considerable interest. These interrelationships were investigated by us for several isotherms in the NaI - KI - furfural system [1]. The NaI - KI - methanol system was investigated by an analogous method. The influence of arginine upon the NaI - KI - methanol system was tested at 30°.

Preparations of NaI and KI that were shown by analysis to be chemically pure and anhydrous were used for the investigation. The methanol, after dehydration and distillation, was absolute, with a sp. gr. of 0.79 and a b.p. of 65°. Isotherms were investigated at 10, 20, 30, and 40° for the ternary system NaI - KI - methanol.

The initial systems, which differed in respect of their concentrations of the components, were placed in small reaction flasks (60 ml) with ground glass stoppers. The flasks were attached to a conical-rotation agitator specially designed by us and were immersed together with the latter in a water thermostat. All tests were run with the system kept in the thermostat for 4 hours. The temperature required for each isotherm was maintained in the thermostat by a very simple nonrelay thermoregulator of our own design [2]. The temperatures of 10 and 20° were maintained in the thermostat by simultaneously hooking up a heating and a cooling system.

The ternary system NaI - KI - methanol was investigated by analyzing the composition of the initial system, the solution, and the solid phase. The test

samples required for analysis of the solution (kept in the thermostat) were taken by means of a special pipette fitted with a rubber bulb. The weighed batches used for investigation of the solution were weighed in a crucible, after which the methanol was evaporated out of the solution, and the latter was calcined for 2 or 3 minutes. As was established, this calcining facilitates the complete removal of the methanol, which would be highly undesirable for the subsequent investigation of the fusion of the mineral mixture residue. The residue of the mineral mixture of NaI and KI was weighed and then subjected to analysis to determine the percentage of each component. As was stated in our previous paper [1], the amounts of NaI and KI were determined by the method of extracting the NaI with alcohol, [3].

EXPERIMENTAL

Four isotherms at 10, 20, 30 and 40° were investigated for the ternary system NaI - KI - methanol. Each isotherm was plotted at five or six points that differed in the proportions of the constituents of the initial system.

In the initial system, the composition of the solution was analyzed after the corresponding equilibrium had been established. The composition of the solid phase was established by computation and was checked graphically by the Schreinemakers' method [4].

The data for the solubility of NaI and KI in methanol at 10, 20, 30 and 40° are listed in tables 1, 2, 3, and 4, respectively, and are reproduced graphically in Figs. 1-4.

Owing to the fact that all the isotherms were investigated at fairly high concentrations, there was no basis for a determination of the equilibrium of the salt system as a product of the solubility, not even for complete ionization. In Tables 1-4 the gross concentrations are listed, since it was found impossible to compute the active concentrations from the data of the analytical method.

In the triangles, the line AB is the solubility curve; and the line CD is the composition curve of the original system. The lines joining the points

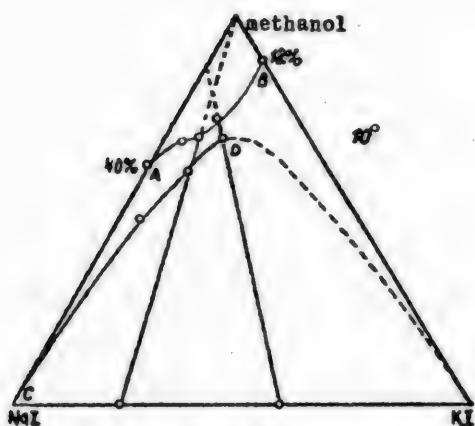


Fig. 1

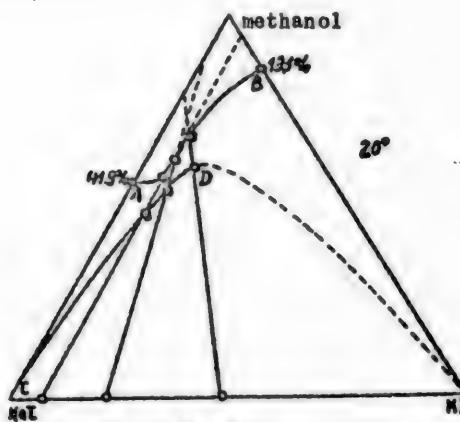


Fig. 2

of the original system to the corresponding points on the solubility curve are connecting straight lines. The connecting lines cannot be parallel because they always intersect. Numerous investigations of salt equilibria of aqueous solutions show the intersection of the connecting straight lines above the CD curve. In this case, their intersection at one of the apexes of the base of the triangle determines the solid phase as a pure component; their intersection on the base line determines the solid phase as a binary system; their intersection within the triangle determines the solid phase as a ternary system; and, lastly, an intersection of the connecting straight lines outside the triangle determines the solid phase as a solid solution.

Nonaqueous solutions furnish another picture. As in the investigation of furfural solutions [1], the connecting straight lines intersect but above the solubility curve AB instead of beyond the line CD in the investigation of a methanol solution as well. In this case the connecting straight lines intersect

Table 1
NaI - KI - Methanol System
10° Isotherm

Serial No.	Initial system (%)			Composition of solution (%)			Solid phase (%)	
	NaI	KI	methanol	NaI	KI	methanol	NaI	KI
1	-	15.0	85.0	-	12.0	88.0	-	100.0
2	17.69	12.38	69.93	17.7	7.2	75.1	41.95	58.05
3	30.53	9.16	60.31	24.5	8.0	67.5	81.66	18.34
4	47.9	4.79	47.31	28.2	5.7	66.1	100.0	-
5	60.0	-	40.0	40.0	-	60.0	100.0	-

Table 2
NaI - KI - Methanol System
20° Isotherm

Serial No.	Initial system (%)			Composition of solution (%)			Solid phase (%)	
	NaI	KI	methanol	NaI	KI	methanol	NaI	KI
1	-	15.0	85.0	-	13.1	86.9	-	100.0
2	29.7	11.85	58.45	26.4	7.1	66.5	54.0	46.0
3	39.21	9.15	51.64	33.4	7.4	59.2	79.3	20.7
4	46.78	7.01	46.21	38.2	7.0	54.8	92.7	7.3
5	60.0	-	40.0	41.9	-	58.1	100.0	-

either at a vertex of the triangle, as a point of a pure solvent (as in the furfural solutions investigated by us) or at one of the triangle's sides (between the point of the pure solvent and the solubility point of one of the components), or finally, within the triangle. In this case the line AB determines the onset of crystallization in a ternary system, and the curve CD is the boundary of complete crystallization. The area above the line AB represents the composition of unsaturated solutions at the given temperature.

Table 3
NaI - KI - Methanol System
30° Isotherm

Serial No.	Initial system (%)			Composition of solution (%)			Solid phase (%)	
	NaI	KI	methanol	NaI	KI	methanol	NaI	KI
1	-	15.00	85.00	14.0	86.00		100.0	
2	29.19	13.21	57.40	25.0	8.6	66.4	56.8	43.2
3	38.7	10.32	50.93	33.0	9.0	58.0	79.9	20.1
4	46.24	8.09	45.65	34.3	9.7	56.0	97.8	2.2
5	52.35	6.28	41.37	37.7	8.3	54.0	100.0	-
6	60.0	-	40.0	44.8	-	55.2	100.0	-

Table 4
NaI - KI - Methanol System
40° Isotherm

Serial No.	Initial system (%)			Composition of solution %			Solid phase (%)	
	NaI	KI	methanol	NaI	KI	methanol	NaI	KI
1	-	16.0	84.0	15.3	83.7		100.0	
2	28.77	14.38	56.85	25.5	8.1	66.4	45.7	54.3
3	38.2	11.46	50.32	32.9	9.2	57.4	73.7	26.3
4	45.72	9.14	44.86	35.7	10.4	53.9	100.0	-
5	51.82	7.25	40.94	37.8	9.1	53.1	100.0	-
6	60.0	-	40.0	46.6	-	53.4	100.0	-

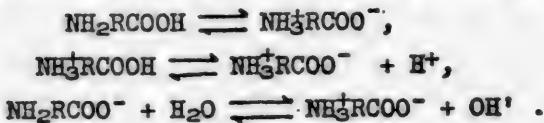
The intersection of the connecting straight lines above the line AB - the region of unsaturated solutions - indicates the presence of solutions whose composition is governed by the composition of the original system. No chemical compounds are formed in the system. In all cases the solid phase is either a pure component or a binary mixture.

As the temperature is raised, the solubility of the NaI - KI increases. The influence of temperature upon the ternary mixture is noticeable in the shift of the region of unsaturated solutions.

According to the researches of Hill, Willson, and Bishop [5], the area of unsaturated aqueous solutions of NaI and KI is much larger than in the case of methanol solutions. The relative solubility of NaI in aqueous and methanol solutions is higher than for potassium iodide.

The arginine was tested in connection with the well-known theory of Bjerrum, supplementing the classical theory, according to which amino acids dissociate in aqueous solutions with the formation of a cation in an acid medium $\text{NH}_2\text{RCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3^+ \text{RCOOH} + \text{OH}^-$ and of an anion in an alkaline medium $\text{NH}_2\text{RCOOH} \rightleftharpoons \text{NH}_2\text{RCOO}^- + \text{H}^+$.

Bjerrum points out the formation of a third form, the double-sign ion. According to Bjerrum, this form develops from the neutral molecule, as well as in the dissociation of the cation and the anion, as in the following equations:



The quantitative relationship of the neutral molecules, the cations, the anions, and the double-sign ions is governed by the pH value of the medium and, in each individual case, by the corresponding isoelectric point of the amino acid.

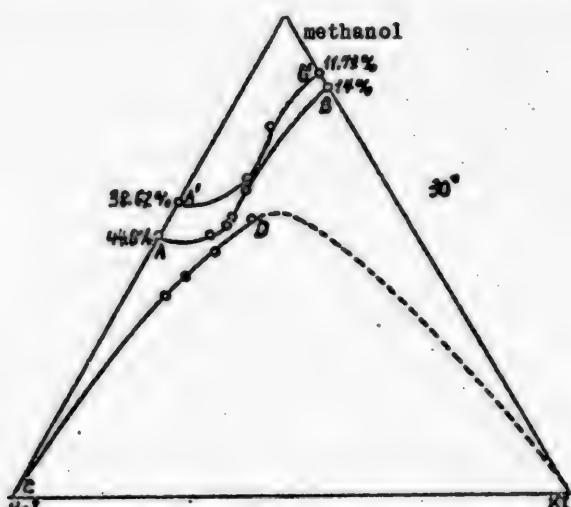


Fig. 3

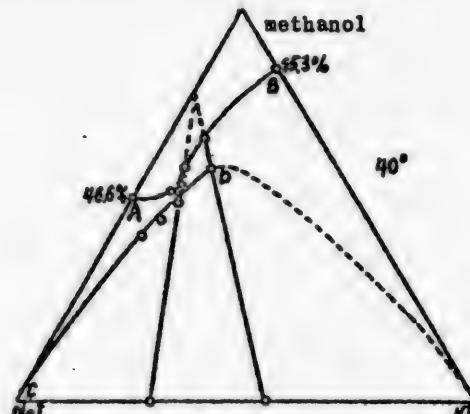


Fig. 4

The polar properties of double-sign ions were established by numerous researchers: O. Bluh [8], A. Thiel and A. Dassler [7], A. Thiel and E. Hern [8], and G. Hederstrand [9]. The increase in the dielectric constant of aqueous solutions of amino acids and the high solubility of electrolytes in aqueous solutions of amino acids were established by the author's researches [10].

The solubility products of BaCO_3 , PbCO_3 , PbSO_4 , PbCrO_4 and Hg_2Cl_2 in aqueous amino acid solutions were considerably higher than in aqueous solutions.

Investigations of the dielectric properties of non-aqueous solutions [10] have established that the dielectric constant of the solution is lower than the dielectric constant of the pure solvent. This indicates the predominance of neutral molecules and of single-sign ions of the amino acids. The double-sign ions are either entirely absent or are present in negligible quantities in non-aqueous solutions of amino acids. Of interest in this connection is an investigation of nonaqueous solutions of the amino acids as solvents for electrolytes.

We tested the influence of arginine at the 30° isotherm of NaI - KI - methanol. The arginine was added to saturation to the ternary NaI - KI - methanol system. The arginine was kept in ampoules. Its moisture content was 0.25% by analysis. The nitrogen content was 26.61 by Kjeldahl. M.p. = 220°. In spite of the negligible solubility of arginine in pure methanol (some 0.1%), the saturation point of arginine when NaI and KI were present varied from 12 to 19%. The introduction of arginine complicated the methods of isotherm investigation somewhat. The weighed batch of the solution used for the test, containing NaI - KI - methanol and arginine, was weighed in a crucible, after which the methanol was evaporated from the solution. The arginine was eliminated by calcining the NaI - KI - arginine residue to constant weight. The crucibles were calcined up to 20-30 minutes. Prolonged calcining made the subsequent separation of the NaI from the KI by the method of alcohol extraction considerably more difficult, as the NaI - KI mineral mixture fused upon prolonged calcining and took much more time to dissolve in alcohol.

The equilibrium of the ternary NaI - KI - methanol system at 30° in the presence of arginine is shown in Table 5. The relative displacement of the solubility curve is shown in Fig. 3. In the triangle: AB is the solubility curve for the NaI - KI - methanol system without arginine; A'B' is the solubility curve with arginine present. Since A'B' is located in the area of unsaturated solutions with respect to AB, the solubility of NaI, KI, and mixtures of the two in methanol in the presence of arginine is lower than in pure methanol.

Table 5
NaI - KI - Methanol System, Saturated with 12% to
19% of Arginine

30° Isotherm

Serial No.	Initial system (%)			Composition of solution %			Solid phase (%)	
	NaI	KI	methanol	NaI	KI	methanol	NaI	KI
1	-	15.0	85.00	-	11.8	88.2	-	100.00
2	29.19	13.21	57.4	14.1	8.6	77.3	73.3	26.7
3	38.7	10.32	50.98	24.4	8.2	67.4	83.1	16.9
4	60.0	-	40.0	38.6	-	61.4	100.0	-

The lowering of the solubility of NaI - KI due to arginine is confirmed by the investigation [10] of the lowering of the dielectric properties of methanol solutions of the amino acids. Thus, the amino acids may be used to level out the solubilities of mineral compounds, depending on the solvent employed.

SUMMARY

1. The isotherms of saline equilibrium of the NaI - KI - methanol system were investigated at 10, 20, 30, and 40°.
2. The influence of arginine on the NaI - KI - methanol system was investigated at 30°. It was established that the solubility of NaI, KI, and their mixtures in methanol is less when arginine is present than in the pure methanol.

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SEPARATION OF RACEMIC GLYCOLS OF THE ACETYLENE SERIES INTO OPTICALLY ACTIVE ISOMERS

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There is no report in the literature on the separation of acetylenic glycols into their optically active components. The only report we possess is the separation of the isomers of an acetylene alcohol, propenyl-ethynyl-carbinol, reported in 1945 in a paper by Kenyon [1].

The subjects of our paper were two acetylenic glycols, diphenyl-butinediol, $C_6H_5-CHOH-C\equiv C-CHOH-C_6H_5$, and dimethylphenyl-butinediol, $(CH_3)_2COH-C\equiv C-CHOH-C_6H_5$. The first of these, synthesized by Z. Lotsch [2], contains two asymmetrical carbon atoms and is correspondingly obtained as a mixture of two isomers, which were isolated in the pure state by Dupont [3]. One of these isomers fuses at 142° , the other at 103° . We decided to begin our investigation with the first, because, on the one hand, it is formed in large quantities, and on the other racemic isomers usually fuse at higher temperatures than inactive ones owing to internal compensation. Our expectations were borne out; this isomer actually turned out to be racemic, which spared us the necessity of investigating the second one. We performed the separation by the method developed by Pickard [4]: the synthesis of the acid phthalate and the crystallization of the latter's cinchoninate. The acid phthalate of diphenyl-butinediol was prepared by reacting phthalic anhydride with the glycolate, prepared by dissolving metallic potassium (1 atom) in diphenyl-butinediol (1 mole). It consists of crystals with a m.p. of $150-151^\circ$. This ester was used in preparing the cinchoninate, which was then subjected to 6 or 7 fractional recrystallizations. To obtain the optically active phthalate, each fraction was treated with a 4% solution of hydrochloric acid, after which the ester was saponified by heating it to $70-80^\circ$ over a water bath with sodium bicarbonate. After double recrystallization from alcohol, the 1-isomer of the glycol produced the following specific rotation in chloroform: $[\alpha]_D^{14} -33.3^\circ$, whereas the dextro isomer had the specific rotatory power of $[\alpha]_D^{14} +30.0^\circ$. It should be noted that the dextro isomer dissolves better during fractional crystallization and therefore remains in solution and is obtained in a less pure state. In spite of all our precautions the glycol resinified somewhat and was hard to purify, which is why it did not fuse sharply - at $141-144^\circ$. The rotatory power was weaker in acetone: -25.0° and $+21.6^\circ$. These figures confirm the observations made by Rule [5]; according to the latter the rotatory power is smaller in solvents with a high dipole moment: in chloroform $\mu \cdot 10^{-8}$ is 1.10, and in acetone 2.71.

* Deceased

Together with the monophthalate of diphenyl-butinediol we obtained a very small quantity of the diphthalate, which was easy to separate because of its low solubility in the ester. It consists of crystals with a m.p. of 159-161°. Its salt with two molecules of cinchonidine was prepared, after which the salt was separated into three fractions by dissolving it in chloroform and precipitating it with petroleum ether. We thus obtained as the first fraction a dextro ester with a specific rotatory power of $[\alpha]_D^{15} +30^\circ$, whereas the second fraction possessed a specific rotatory power of -40° . Let us note in passing that cinchonidine is laevo rotatory in chloroform. The optically active diphthalate of diphenyl-butinediol fused at 159-163°.

We separated dimethyl-phenylbutinediol into its optically active isomers by two methods - via the cinchoninate of the acid phthalate and by crystallization from an optically active solvent (bornyl acetate).

The phthalate of dimethyl-phenyl-butinediol was prepared by letting potassium glycolate act on phthalic anhydride. Owing to the tendency of the glycolate to resinify, its preparation, as well as its reaction with phthalic anhydride, was effected in the cold in an ether medium for 25-30 hours with constant stirring. The potassium salt of the acid phthalate was dissolved in a large amount of benzene and decomposed by 10% hydrochloric acid. After purification, the acid ester consists of small crystals with a m.p. of 137-138°. The same ester was prepared by heating the glycol with phthalic anhydride and pyridine. From it we prepared the cinchonin salt, which was likewise subjected to repeated recrystallization from chloroform. The first fraction's crystals are laevo rotatory, the last ones are dextro rotatory. The optically active phthalate recrystallized twice from the ethyl acetate fused at 142-144°. The specific rotatory power of the dextro isomer is: $[\alpha]_D^{15} +12^\circ$; and of the laevo is -12.5° .

To obtain the glycol, the optically active phthalate was saponified by heating to 70-80° for 10 minutes with sodium bicarbonate. The glycol fused at 74-77°. Its specific rotatory power was determined in chloroform and acetone. The results obtained were as follows: in chloroform $[\alpha]_D^{20} +16.5^\circ$ and -16.5° ; in acetone $+16^\circ$ and -16° . Thus, here too, the rotatory power in chloroform is higher than that in acetone, though in this case the difference is less striking. It is of interest to note that the rotatory power of the diphthalate of diphenyl-butinediol is nearly twice as large as that of the corresponding ester of dimethyl-phenyl-butinediol. According to van't Hoff's rule, the rotatory power of compounds with several centers of asymmetry is the sum of the rotatory powers corresponding to the several centers. This rule is confirmed by the example of our esters, which are closely, though not fully, related in structure.

The separation of racemic isomers into their optically active components was the subject of several investigations, which yielded positive as well as negative results. Thus, the endeavors to separate carvoxime into d and l forms by dissolving it in limonene [6] ended in failure, as did the efforts to separate camphocarboxylic acid by means of the same solvent [7]. But Schöer [8] in his endeavors to separate racemic amygdalic acid by shaking it up with water and optically active carvol, did succeed. This requires that some sort of link be formed between the solute and the active solvent, some adsorptive or chemical (even though unstable) compounds. In this case these compounds of the active solvent with the d and l forms were of a diastereoisomeric nature, and, hence, possessed various properties of the derivatives. It seemed to us

that such compounds could be formed whenever a hydrogen bond can arise.

In Schöer's experiments a bond of this sort could be formed at the expense of the oxygen of the ketone group of the carvol and the carboxyl hydrogen of the amygdalic acid. There are no data indicating a hydrogen bond in limonene as a solvent, which may possibly explain why no success was had with this solvent. Unfortunately, the investigation of the behavior of racemic compounds in optically active solvents has been far from adequate up to now, so that no definite statement can as yet be made thereon.

In our experiments on the separation of the dimethyl-phenyl-butinediol into its optically active components we employed bornyl acetate as the solvent. Here the hydrogen bond could be formed at the expense of the hydroxyl hydrogen of the glycol, and the acetyl oxygen of the bornyl acetate. In fact, fivefold recrystallization from laevo bornyl acetate enabled us first to isolate the laevo and then the dextro isomer of the glycol. The rotatory power was weak: -0.10° in chloroform for one fraction, and +0.05° and 0.07° in the other. To prove that this rotation does not depend upon the residual traces of the bornyl acetate, we recrystallized the active glycol four times from alcohol; analysis of the mother liquor indicated the complete absence of activity and, hence, the complete elimination of the bornyl acetate. The active glycol produced fused at 76-77°.

EXPERIMENTAL

Acid phthalate of diphenyl-butinediol, $C_6H_5-\text{CH}(\text{OCOC}_6\text{H}_4\text{COOH})-\text{C}\equiv\text{C}-\text{CHOH}-C_6H_5$. To a solution of 9 g of diphenyl-butinediol (m.p. = 142) in 100 ml of anhydrous ether 1.4 g of metallic potassium, previously shaken up in powdered form with hot xylene, was added. The mixture was then placed in a flask connected to a reflux condenser and subjected to mechanical stirring for 8 hours. The potassium dissolved, and potassium glycolate precipitated out, accompanied by some resinification. Then 5.5 g of phthalic anhydride was added, whereupon the glycolate entered into solution. The mixture was stirred for 15 hours. The precipitate of the potassium salt of the acid ester was rapidly filtered out and dissolved in 150 ml of benzene, and the solution was then shaken up with 75.5 ml of 0.1 N sulfuric acid. The layer of benzene was removed and dried with sodium sulfate, after which the benzene was driven off in vacuum at room temperature. The residue is a tenacious yellow mass, from which a few crystals were separated out. This mass was dissolved in acetone; 48 hours later white crystals were thrown down; these crystals were separated out, washed with benzene and twice recrystallized from ether, in which part of the product did not dissolve. As will be indicated below, this insoluble product was the di-phthalate of diphenyl-butinediol. The crystals obtained from the ether fused at 149-151°, and at 150-151° after two more recrystallizations from acetone. Yield = 2 g (13.8% of the theoretical).

0.2038 g substance: 0.5856 g CO_2 ; 0.0845 g H_2O .
0.0050 g substance: 0.1072 g camphor: Δt 5.0°.

Found %: C 74.65; H 4.70; M 373.2
 $\text{C}_{24}\text{H}_{18}\text{O}_5$. Calculated %: C 74.58; H 4.43; M 386.1.

Upon titration, 0.3708 g of the substance required 2.15 ml of a KOH solution (T. 0.02580).

$\text{C}_{23}\text{H}_{17}\text{O}_3\text{COOH}$. Calculated 2.09 ml KOH.

Upon gradual heating the acid phthalate of the glycol phthalic anhydride is sublimed.

Cinchoninate of the acid phthalate of diphenyl-butinediol. 1 g of the acid phthalate and 0.81 g of cinchonin were heated in chloroform for 30 minutes until all the cinchonin dissolved. Upon cooling a transparent syrupy deposit settled out of the solution. The chloroform was decanted, and 10 ml of petroleum ether was added to the residue. Upon rubbing with a stick, we got small white crystals of the cinchoninate, with a m.p. of 82-84°.

0.0359 g substance: 1.3 ml N₂ (12°, 776 mm).

Found %: N 4.37.

C₄₃H₄₀O₆N₂. Calculated %: N 4.12.

Optically active phthalates of diphenyl-butinediol. 2 g of the cinchoninate of the acid phthalate of diphenyl-butinediol were dissolved with heating in 10 ml of carbon tetrachloride and then cooled in a freezing mixture. Part of the salt precipitated as a transparent resinous mass. The filtrate was evaporated to a volume of 5 ml, and the salt was precipitated from it by petroleum ether. The fractions obtained were again dissolved and fractionally precipitated by petroleum ether. Six fractions were thus obtained. Each of them was dissolved in 5-7 ml of chloroform and treated with a 4% solution of hydrochloric acid. The chloroform solution was dried with calcined sodium sulfate and then evaporated. To determine the direction of rotation 1 ml of the solution of each fraction was diluted with chloroform to a total of 5 ml. The following results were obtained:

Fraction No.:	1	2	3	4	5	6
Rotation in °:	-0.05	-0.16	-0.18	+0.09	+0.13	+0.1

The first three fractions weighed 0.35 g, and the last three 0.25 g. To determine the specific rotatory power, weighed batches of 0.2 g of the dextro- and laevo-rotatory esters were dissolved in 5 ml of chloroform. The laevo ester had a rotation of -0.16° and -0.17°; the dextro ester had a rotation ranging from +0.14° to +0.16°. From this the specific rotatory power was computed as -16.5° for the laevo ester and +15° for the dextro ester.

Optically active diphenyl-butinediols. 0.2 g of the laevo-rotatory phthalate was dissolved in 5 ml of chloroform, 5 ml of a 5% solution of sodium bicarbonate was added to the mixture, and the latter was then heated to 70-80° with constant stirring. The chloroform solution was removed and dried, after which 0.12 g of glycol was obtained after the solvent was driven off. This was then dissolved in 5 ml of chloroform, and the rotatory power, which was found to be laevo, was then determined in this solution. The chloroform was then driven off and the residue dissolved in 5 ml of acetone, the solution then being again tested in the polarimeter. This treatment was also given the dextro-rotatory phthalate of diphenyl-butinediol, from which the dextro isomer of the glycol was prepared. The results are listed in Table 1.

Table 1

Solvent	Temperature in °	Displacement angle		Specific rotation in °	
		<u>l</u>	<u>d</u>	<u>l</u>	<u>d</u>
Chloroform	14	0.20	0.18	-33.3	+30
Acetone	15	0.15	0.13	-25	+21.6

The optically active glycol recrystallized from alcohol and acetone fused at 141-144°.

Diphthalate of diphenyl-butinediol and its separation into its optically active components. It was mentioned above that some of the diphthalate was formed during the preparation of the monophthalate of diphenyl-butinediol,



which is insoluble in ether, but is easily soluble in acetone, benzene, and chloroform. 0.5 g of it was obtained (2.25% of the theoretical). It fused at 151-152° after two recrystallizations from acetone.

0.2069 g substance: 0.5471 g CO₂; 0.06780 g H₂O.

0.1582 g substance: 13.56 g benzene: At 0.11°.

Found %: C 72.12; H 4.20; M 541

C₃₂H₂₂O₈. Calculated %: C 71.89; H 4.15; M 534.2.

A mixture of 0.3 g of the diphthalate, 0.36 g of cinchonidine, and 5 ml of chloroform was boiled for 30 minutes until fully dissolved. Upon cooling the salt was precipitated as a syrupy mass, which is converted into a finely crystalline white powder by the addition of petroleum ether and rubbing with a stick. Yield = 0.5 g (93.9% of the theoretical); m.p. = 90-92°.

0.0722 g substance: 3.4 ml M₂ (20°, 735 mm).

Found %: N 5.15.

C₇₀H₆₆O₁₀N₄. Calculated %: N 5.0.

The salt of cinchonidine and the diphthalate (0.5 g) was dissolved in 10 ml of chloroform, with heating, and the solution was placed in a freezing mixture. The precipitate was filtered out, and the filtrate evaporated to a volume of 5 ml; the salt was precipitated from the latter by petroleum ether. This yielded 0.2 g each of 2 fractions of crystals. Each fraction was dissolved in 5-7 ml of chloroform and shaken up with 4% hydrochloric acid. The chloroform solution of the first fraction was dried with sodium sulfate, and after the chloroform had been driven off, 0.1 g of the acid phthalate remained; the corresponding figure for the second fraction was 0.095 g. Each fraction was dissolved in 5 ml of chloroform; the rotatory-power determinations yielded the following results.

	Angle of rotation in °	[α] _D ¹⁵
First fraction	+0.15	+30°
Second fraction	-0.19	-40°

The optically active ester exhibited an acid reaction with litmus paper and fused at 159-163°.

Phthalate of dimethyl-phenyl-butinediol, (CH₃)₂COH-C=C-CH(OCOC₆H₄COOH)-C₆H₅. Dimethyl-phenyl-butinediol was prepared by the method developed by Y. Zalkind and A. Ivanov [9]; its m.p. was 76.6°. To a solution of 10 g of this glycol in 50 ml of absolute ether 2 g of pulverized potassium shaken up with hot xylene was added. At the start the reaction produced heating, and the mixture had to be cooled with ice water. After the glycolate had been thrown down, 7 g of phthalic anhydride was added to the mixture and it was stirred for 20 hours. The further treatment was the same as that used to prepare the phthalate of diphenyl-butinediol. Yield of the crude product = 7 g (39.35% of the theoretical),

This ester was also prepared by another method. 15.2 g of dimethyl-phenyl-butinediol, 11.5 g of phthalic anhydride, and 10 ml of pyridine were heated to 60-65° for one hour and a half, after which the mixture was allowed to stand for 48 hours. The mixture was then shaken up with 70 ml of a 10% solution of hydrochloric acid, and the product of the reaction was extracted with ether. After the ether had been driven off, there remained 22 g (81.2% of the theoretical) of crystals, which fused at 137-138° after being twice recrystallized from ethyl acetate - this is the same m.p. as was obtained by the previous method.

0.1572 g substance: 0.4104 g CO₂; 0.0811 g H₂O.

0.0095 g substance: 0.1029 g camphor: Δ⁺. 10.4°.

Found %: C 71.20; H 5.77; M 355.1.

C₂₀H₁₈O₅. Calculated %: C 70.97; H 5.57; M 338.1.

In titration, 0.1465 g of the substance required 90.85 ml of a NaOH solution (T. 0.1877).

C₁₉H₁₇O₃COOH. Calculated: 90.92 ml.

Cinchoninate of the acid phthalate of dimethyl-phenyl-butinediol. 3 g of the acid phthalate was dissolved in 15 ml of carbon tetrachloride, and 2.6 g of cinchonin was added to the solution. The mixture was boiled over a water bath for 30 minutes, after which it was cooled. Within 2 hours a precipitate was thrown down; the precipitate was separated out, dissolved in carbon tetrachloride, and reprecipitated with petroleum ether. After this purification treatment had been performed three times, the salt fused at 79-81°.

0.1200 g substance: 4.8 ml N₂ (21°, 754 mm).

Found %: N 4.72.

C₃₉H₄₀O₈N₂. Calculated %: N 4.43.

The cinchoninate is easily soluble in chloroform, alcohol, and acetone, but poorly soluble in water.

5 g of the cinchoninate was dissolved in 15 ml of chloroform, with heating. Upon cooling with a freezing mixture 0.7 g of the salt was thrown down. The mother liquor was precipitated with petroleum ether. Six more fractions were obtained in the same fashion. Each fraction was again dissolved in chloroform and treated with 4% hydrochloric acid. The chloroform solution was dried with sodium sulfate, and the chloroform driven off. A 0.2 g weighed portion of the dimethyl-phenyl-butinediol phthalate fraction was taken and its rotatory power determined in a chloroform solution. The results obtained are listed in Table 2.

The first 4 fractions (1.2 g) were combined and recrystallized from ethyl acetate; the same was done with the last three fractions (0.5 g). The optically active phthalate of dimethyl-phenyl-butinediol fused at 142-144°. 0.2 g of each isomer was dissolved in 5 ml of chloroform for the determination of the specific rotatory power. The results were as follows:

for the d isomer [α]_D¹⁵ +12.5°; for the l isomer [α]_D¹⁵ -12°.

Optically active dimethyl-phenyl-butinediols. Weighed portions of 0.5 g of each isomer of the phthalate were dissolved in chloroform and treated with

a 4% solution of sodium bicarbonate for 10 minutes at 60-70°. The chloroform solution was dried with sodium sulfate. Driving off the chloroform left glycol with a m.p. of 74-77° as a residue. Solutions of 0.2 g of each isomer in 5 ml of chloroform and in 5 ml of acetone were prepared to measure the rotatory power. The results obtained were as follows:

In chloroform.....l isomer -16.5°; d-isomer +16.5°.

In acetonel isomer -16°; d-isomer +16°.

Table 2

Fraction No.	Weight of fraction		$[\alpha]^{15}_D$
	Cinchoninate g	After acid treatment of the salt	
1	0.70	0.30	-0.11°
2	0.80	0.38	-0.12
3	0.70	0.30	-0.14
4	0.05	0.2	-0.07
5	0.5	0.2	+0.10
6	0.5	0.2	+0.13
7	0.45	0.15	+0.14

Separating the racemic isomer of dimethyl-phenyl-butinediol by the use of a solvent. As an optically active solvent we used laveo-rotatory bornyl acetate. 2 g of dimethyl-phenyl-butinediol was dissolved in 5-7 ml of the anhydrous bornyl ester; the mixture was heated until the crystals were completely dissolved, and then gradually cooled. As soon as the first crystals appeared they were rapidly separated out and washed with ether. Five fractions were thus obtained. Each fraction of the crystals was recrystallized from chloroform, ether, and alcohol. The final mother liquor exhibited absolutely no rotation of the plane of polarization and, hence, contained no traces of bornyl acetate. The m.p. of the glycol was 76-77°. 0.2 g of each fraction was dissolved in 5 ml of chloroform to determine the rotatory power. The results are listed in Table 3.

Table 3

Fraction No.	Angle of rotation	$[\alpha]^{20}_D$
1	From -0.03 to -0.05°	From -3.2 to -5
2	From -0.07 to -0.08°	From -7 to -8
3	From -0.08 to -0.10	From -8.2 to -10
4	From -0.08 to -0.09	From -8 to -9
5	From +0.05 to +0.07	From +6 to +7

The figures of Table 3 indicate that the racemic isomer was actually separated, though not enough so as to produce optically active glycals in pure state.

SUMMARY

Two acetylenic racemic γ -glycols, diphenyl-butinediol (m.p. = 142°) and dimethyl-phenyl-butinediol were separated into their optically active components. The optically active isomers of the mono- and diphthalates of diphenyl butinediol and the phthalate of dimethyl-phenyl-butinediol were likewise prepared. The feasibility of separating the racemic isomer of dimethyl-phenyl-butinediol into its optically active components by fractional crystallization from optically active bornyl acetate was demonstrated. The supposition was expressed that the separation of the racemates by crystallization from optically active solvents is bound up with the possibility of forming a hydrogen bond between the molecules of the racemate and the solvent.

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THE STRUCTURE OF NITROSYL CHLORIDE AND ITS CONDENSATION REACTIONS WITH THE OLEFINS

A. Y. Yakubovich and A. L. Lemke

The constitution of nitrosyl chloride is schematically represented by the general formula (I) with homopolar bonds. The actual constitution of this substance is more adequately represented, however, by structural formulas that allow for electron interchange within the molecule.

From this standpoint it is probable that in the NOCl system of atoms the structure (I) coexists with such resonance ionization structures as (II) and (III):



Since the ionization structure may govern the general course of the interactions in many chemical reactions, the problem of the relative importance of these various structures becomes one of considerable importance.

An idea of the relative importance of the internal ionization structures (II) and (III) in the NOCl molecule may be gained from the following physico-chemical properties and the data on the structure of inorganic nitrosyl compounds.

As far back as 1909, Hantzsch [1], in his study of the change in molecular weight and electrical conductivity of solutions of nitrosyl perchlorate and sulfate, the general formula for which, like that for nitrosyl chloride, may be expressed by X-N=O, where X is the acid radical, in which the hydrogen is replaced by the nitroso group, assumed the existence of the unusual NO cation in these compounds.

This assumption was subsequently confirmed by the Raman spectroscopic investigations of Angas and Leckie [2], who found a characteristic frequency due to the NO group in nitrosyl perchlorate and sulfate.

In their study of the structure of nitrosyl chloride by the electron diffraction method, Ketelar and Palmer [3] found the following constants for its molecule, which lead us to compare them with the known constants for other nitroso-derivative acids and oxides of nitrogen. In the latter, according to Pauling, the O and N atoms are linked together by double and triple electron bonds, i.e., by a sum total of bonds that is a multiple of two (see table).

Analyzing the data obtained for interatomic distances, Ketelar and Palmer come to the conclusion that the observed increase in the N - Cl distance, together with the decrease in the N - O distance, as compared with the computed values is the result of the superposition of structures I and II. Comparison of other constants of nitrosyl chloride and other nitroso acids and oxides of nitrogen yields analogous results.

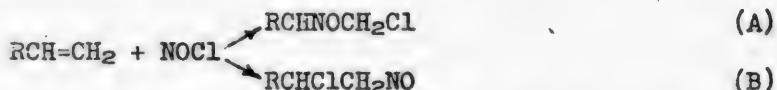
Thus, all the data on compounds of the X-N=O type, where the nitroso group replaces the hydrogen in the HX acid molecule, indicate that the actual structure of the nitrosyl chloride molecule is most probably represented by the superposition of structures I and II..

Compound	Distance (measured) Å		Sum of covalent radii (computed) Å		Frequency of N-O bond (measured) in cm ⁻¹ for indicated structures	
Nitrosyl perchlorate or sulfate	-	-	N≡O	1.06	N≡O ⁺	2330
Nitrosyl chloride	N=O	1.14±0.02	N=O	1.18	N=O ⁺	1832
Nitric oxide	N=O	1.14±0.02	-	-	N=O	1892

The behavior of nitrosyl chloride in the well-known nitrosation reactions of organic compounds with an active (or putting it differently, positive) hydrogen atom is in good agreement with the outlined structure of this molecule.

We were interested in how nitrosyl chloride would behave in addition reactions with asymmetrical ethylenic molecules.

The generally accepted homopolar structure of nitrosyl chloride gives no indication of how the addition reaction might proceed in such cases. The only assumption we can make is that the products of the addition of nitrosyl chloride to olefins of the RCH=CH₂ type could be (A), or (B), or (A) and (B) in unknown proportions:



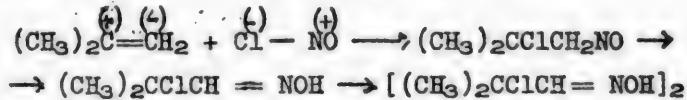
It follows from the well-known Markownikoff's rule on the addition of halogen acids to olefins, expressed in the terminology of electron concepts of the structure of matter, that the positively polarized atom (hydrogen) moves toward the negative carbon atom, whereas the negative radical (the halogen) moves toward the positive carbon atom.

Markownikoff's rule, naturally enough, is inapplicable to nitrosyl chloride, but if it is admitted that in the addition reaction to the ethylene bond of an asymmetrical molecule the direction the reaction will take is governed by the polarity of the reacting bonds of the reaction components, as is the case with the halogen acids, we must look for a definite direction of the

addition reaction in the case of nitrosyl chloride as well - depending upon the internal ionization structures of the reagents. In the case of nitrosyl chloride the chlorine atom must become attached to the positive carbon atom, whereas the NO group is attached to the carbon atom with a denser electron shell.

The well-known addition reactions of nitrosyl chloride to the ethylene hydrocarbons confirm this hypothesis. Thus, for example, isobutylene reacted with nitrosyl chloride yields an oxime of chloro-isobutyraldehyde, according to Ipatieff [4]. This trend of the reaction is dictated by the polarity of the reacting ethylene and N-Cl bonds. As the reaction we are considering proceeded in such a way that the nitrosyl chloride was obtained directly from the reaction mixture (a mixture of amyl nitrite and isobutylene was formed upon cooling with hydrochloric acid), we resolved to repeat it, using ready nitrosyl chloride. It was found that the principal reaction product (yield was 50% of the theoretical) was the same substance as in the reaction described by Ipatieff, but it had a somewhat higher melting point (103-104°, as against 97° according to Ipatieff) and consisted largely, not of the oxime of chloro-isobutyraldehyde, but of the latter's dimer.

Thus the reaction described may be represented by the following equation, where (+) and (-) indicate merely the qualitative distribution of the density of the electron shell in the reacting bonds:



Naturally, the polarity of the reacting bonds can merely facilitate the course of the reaction in certain directions, accelerating it but by no means preventing reactions that follow another course. In the case under consideration, more particularly, we get, in addition to the oxime mentioned, a minute quantity of a product that apparently is 1-chloro-2-nitro-2-methylpropane. It is probably formed as a result of the oxidation of the intermediate nitroso compound, which is formed as follows:



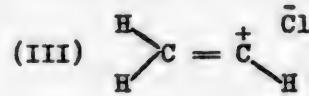
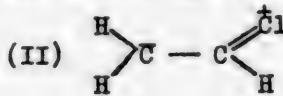
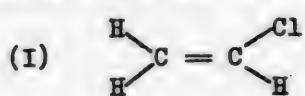
The addition of NOCl to the allyl chloride takes place in a wholly analogous manner, i.e., in accordance with the polarity of the reacting bonds. In this case, the end product of the reaction is 1,2-dichloro-3-nitropropane (yield = 55%), which is formed as a result of the oxidation of the intermediate nitroso compound by the nitrosyl chloride.



In this reaction, the nitrosyl chloride is decomposed, liberating nitrogen and chlorine [5], which, added to the allyl chloride, forms 1,2,3-trichloropropane, which was likewise isolated from the reaction mass.

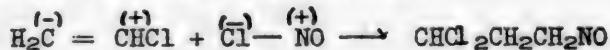
The considerably more abrupt polarity of the ethylene bond will be expressed in the chlorinated derivatives of ethylene, since in this case the superposition of the resonance structures with a positive halogen atom, as for example, in the case of vinyl chloride, will increase the density of the electron shell about the carbon attached to the hydrogen atoms, while the superposition of a

structure with a C-Cl ionization bond will reduce the density of the electron shell about the carbon attached to the halogen:

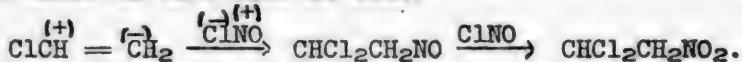


To sum up, the ethylene bond is polarized in such a way as to make the carbon attached to the hydrogen atoms negative, while the positive end of this bond's dipole is located at the carbon atom attached to the halogen.

Hence, when the nitrosyl chloride is added to vinyl chloride or vinylidene chloride we should expect reactions that would take the following course exclusively or nearly exclusively:

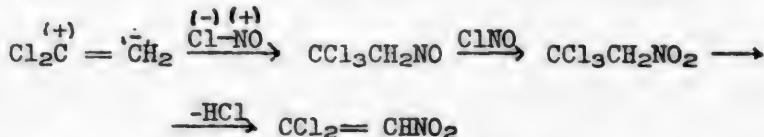


Experiment has shown that with vinyl chloride the reaction products obtained as 1,1-dichloro-2-nitroethane (yield 20%), trichloroethane, an appreciable quantity of chloroacetic acid, with as much as 35% by weight of the resultant mixture consisting of tar. Since the tar is probably formed, not as a result of changes in the products of the nitrosyl chloride addition reaction, but owing to the polymerization and oxidation of the vinyl chloride, the major trend of the NOCl addition reaction turns out to be subject to the polarity of the reaction bonds in this case as well:



The way in which the chloroacetic acid is formed is not entirely clear.

The condensation of vinylidene chloride is more complicated. The end products of the reaction are asymmetrical tetrachloroethane, and 1,1-dichloro-2-nitroethylene. In this case the reaction apparently is:

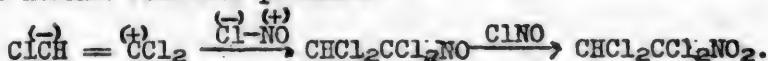


and, as usual, it is accompanied by the chlorination of the original olefin, with the formation of tetrachloroethane.

Thus, the addition of nitrosyl chloride takes place normally in this condensation reaction as well.

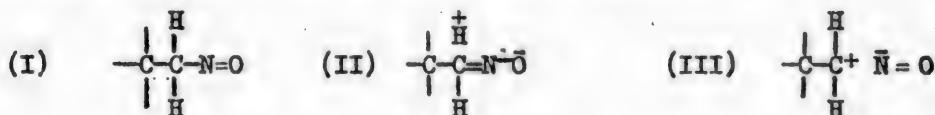
The condensations described above are relatively rapid (12 to 48 hours) at room temperature, wherein they differ from the condensation of nitrosyl chloride with trichloroethylene, which yields a product that constitutes an extremely small percentage by weight of the initially charged components, even after the reagents have been in contact with each other for as long as 14 days.

The reactivity of the ethylene bond is sharply reduced, as we know, in trichloroethylene, as is manifested in the extremely low reaction velocity of the addition of nitrosyl chloride to trichloroethylene. Another peculiarity of this reaction, however, is the fact that the addition does not take place in accordance with the polarity of the reacting bonds. Namely, 1,1,2,2-tetrachloro-1-nitroethane (yield 88%), together with pentachloroethane, is formed instead of the normal reaction product:



In this reaction, which is extremely slow, the kinetic effect of the polarity is concealed, and the process takes the more favorable of the two thermodynamically possible courses of the addition reaction.

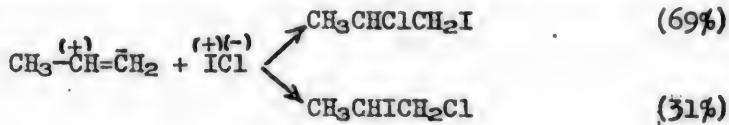
A distinctive trait of the condensation of nitrosyl chloride with halogen derivatives of the olefins, as contrasted with reactions with the ethylene hydrocarbons, consists in the fact that the intermediate nitroso compounds formed do not rearrange into oximes as occurs in the hydrocarbons, but are oxidized to nitro compounds. There is no doubt that here we have an instance of the influence of the two chlorine atoms, which retard the nitroso-oxime rearrangement so appreciably that the oxidation reaction velocity of the nitroso compound becomes much higher than the rearrangement velocity. This influence is probably expressed in the purely electrostatic effect of the strongly negative fields of the chlorine atoms upon the positively polarized hydrogen atom, acting against the field produced by the rearrangement. The latter effect may be represented by the following series of diagrams, corresponding to the structure of the nitroso compounds:



2 structures

The superposition of structure (II) reflects the trend of nitroso compounds toward an oxime rearrangement. When two halogen atoms are attached to the adjacent carbon atoms, the negative field of the former atoms will act upon the H-atom in a direction contrary to the effect of the nitroso group, and the rearrangement will be retarded. The results of our investigation of the addition reactions of nitrosyl chloride, as well as of the addition of the halogen acids to the asymmetric olefins, lead us to conclude that most such chemical processes will tend to follow a course that is chiefly dictated by the polarity of the reacting bonds.

In agreement therewith, for example, is the course of the well-known addition reaction of ICl and propylene, yielding 69% of 1-iodo-2-chloropropane [7]:



EXPERIMENTAL

1. Condensation of Isobutylene with Nitrosyl Chloride

Preparation of the Dimer Oxime of Chloroisobutyraldehyde

(Experimental Work Done by V. A. Shpansky)

30 g of ether, 19.5 g of isobutylene, and 15.0 g of nitrosyl chloride were put into a wide test tube, placed in a Dewar flask containing a freezing mixture at a temperature of -16°. The reagents were allowed to stand for 12 hours, the temperature of the freezing mixture gradually rising during this time to -8°. The reaction resulted in a mixture of a liquid and bluish crystals, which were analyzed separately. The crystals were separated from the liquid, washed with chilled ether, and dried in vacuum. The yield was 15 g of a substance with a m.p. of 102-103°, representing a yield of 50% of the theoretical in terms of the oxime of chloro-isobutyraldehyde. After recrystallization of the substance twice from alcohol, it was isolated as brilliant white crystals with a m.p. of 103-104°. As the melting point of the substance we had prepared did not agree with the melting point of the oxime of chloro-isobutyraldehyde (97° according to Ipatieff), the compound was subjected to elementary analysis.

0.1500 g, 0.0901 g substance: 21.60 g, 21.85 g benzene: $\Delta t^\circ = 0.175^\circ, 0.095^\circ$.
3.840 mg, 3.000 mg substance: 5.500 mg, 4.340 mg CO_2 ; 2.370 mg, 1.840

mg H_2O .

3.372 mg substance: 0.353 ml N_2 (24°, 756 mm)

3.155 mg substance: 0.336 ml N_2 (26°, 756 mm).

9.365 mg, 12.20 mg substance: 3.50 ml, 4.42 ml 0.02 N AgNO_3 .

Found %: C 39.36, 39.41; H 6.97, 6.86;

C 1 28.32, 128.22; N 11.79, 11.93;

M 203.0, 221.9.

$\text{C}_4\text{H}_8\text{ONCl}$. Calculated %: C 39.50; H 6.64; N 11.52; Cl 29.18;

M 121.52.

A sample of the oxime of chloro-isobutyraldehyde prepared by us in accordance with Ipatieff's prescriptions from amyl nitrite and isobutylene in the presence of hydrochloric acid, proved, after double recrystallization from alcohol, to be identical with the substance we had prepared above and fused at 104-105°, instead of 97°, as stated by Ipatieff. A sample containing a mixture of the Ipatieff oxime and the oxime synthesized with nitrosyl chloride gave no depression of the melting point. The molecular weight of the substance described, which is almost twice the molecular weight of the oxime of chloro-isobutyraldehyde, together with the data of the elementary analysis, which agree with the figures computed for this oxime, indicate that the compound is not monomolecular, but is a mixture, most of which consists of the dimer of chloro-isobutyraldehyde with small amounts of the monomer.

Saponification tests of the substance indicate that when 3 g of the substance were boiled for 25-30 minutes with concentrated hydrochloric acid (sp. gr. 1.18), all of it went into solution, the latter turning dark brown in color. The solution, neutralized with solid bicarbonate, was twice extracted with ether. The ether extract was dried with sodium sulfate. After the ether had been driven off, there was left a small quantity of brown oil, which decomposed when we endeavored to distill it in vacuum.

As the above-described saponification experiment was a failure, and it proved impossible to isolate chloroisobutyraldehyde from the saponification products, this experiment was repeated under different conditions.

15 g of the substance mixed with 60 ml of hydrochloric acid were boiled in a flask connected to a straight-run condenser. In the receiver of the condenser there collected, together with hydrochloric acid, 6 g of a heavy oil that was insoluble in the acid. The oil, after drying with sodium sulfate, was redistilled; in this process, some 0.8 g of a liquid with a b.p. of 85-100° was distilled off, this b.p. being close to the b.p. of chloro-isobutyraldehyde (90°, according to Broche), plus a small amount of a higher-boiling fraction (up to 130°). The residue in the distilling flask turned into a dark tarry mass. The 85-100° fraction gave a positive qualitative test for an aldehyde with ammoniacal silver nitrate.

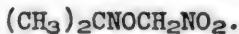
The fact that the yield of chloroisobutyraldehyde is extremely small may be due to either one of two circumstances: a large part of the unstable chloroisobutyraldehyde decomposes when boiled with hydrochloric acid, as we see from the two saponification experiments described above, or the dimer of the oxime possesses a structure that makes the formation of the aldehyde during saponification impossible, and the small quantity of the aldehyde isolated is due to its origin as an impurity in the monomer of the oxime. The latter assumption is more likely, since the determination of hydroxylamine in the saponified weighed portion of the substance (Raschig method) indicated its presence in an amount corresponding to a 10% content of the oxime of chloro-isobutyraldehyde.

The liquid products of condensation, isolated from the crystals as described above, were subjected to vacuum distillation with a dephlegmator, after the ether had been driven off. In this distillation the mixture was divided into two fractions. The residue left in the distilling flask was 2.6 g of a brown viscous mass. The first fraction consisted of 2 g of a dark-blue liquid with a b.p. of 40-55° (at 7 mm), most of which quickly turned into colorless crystals. The colorless crystals formed during the polymerization of the nitroso compound contained in the first fraction were washed with benzene and dried in vacuum.

The substance fuses at 82-84°, turning into a dark-blue liquid. Upon cooling colorless crystals are again formed. It dissolves in aqueous alkalies with slight heating, coloring the solution yellow. Analysis of the alkaline solution for its nitrite-ion content with Griess's reagent and by the method of diazotization of aniline with the solution obtained, and the subsequent coupling with naphthylamine yielded a negative reaction.

3.710 mg, 3.460 mg substance: 4.975, 4.1625 mg CO₂; 2.210 mg, 2.110 mg H₂O.
4.465 mg, 5.715 mg substance: 0.862 ml, 0.884 ml N₂ (29°, 30°, 765 mm).
Found %: C 36.56, 36.45; H 6.70, 6.85; N 21.65, 21.41.
C₄H₈O₃N₂. Calculated %: C 36.35; H 6.11; N 21.20.

The analysis and properties indicated that the substance is a tertiary nitroso compound, the structure of which may be written as follows:



This compound has been described by Sidorenko, who gives its melting point as 80.5° [8].

Upon redistillation in vacuum of the second fraction (3 g of liquid with a b.p. of 55-70° at 7 mm), we were able to isolate a small quantity of a substance with a b.p. of 68-69° (at 6 mm), a colorless liquid with a sharp odor and a d_4^{20} of 1.262. The substance was insoluble in water or in aqueous solutions of alkalis, and is miscible with the usual organic solvents. An abundance of nitric oxide is formed upon pyrolysis. From its properties and the quantitative elementary content, which closely resembles their content in the compound with a formula of $C_4H_8ClNO_2$, this substance probably is impure 1-chloro-2-nitro-2-methylpropane. We were unable to isolate the compound in a chemically pure state owing to the small quantity obtained.

2.760 mg substance: 3.290 mg CO_2 ; 1.330 mg H_2O .
5.558 mg, 7.250 mg substance: 0.480 ml, 0.632 ml N_2 (22.29°, 754 mm).
Found %: C 32.5; H 5.89; N 9.90, 9.79.
 $C_4H_8O_2NCl$. Calculated %: C 34.91; H 5.86; N 10.18.

2. Condensation of Allyl Chloride with Nitrosyl Chloride

Preparation of 1,2-Dichloro-3-nitropropane

8 g of allyl chloride (b.p. = 46°) and 6.9 g of nitrosyl chloride (molar proportion) were placed in each of three chilled tubes which were then sealed. The sealed tubes were allowed to stand at room temperature (16-18°) until the red color of the nitrosyl chloride disappeared. As a rule the reaction ended after 12 to 24 hours; the contents of the tubes took on a slightly greenish color during this time. The tubes were chilled in a mixture of acetone and carbon dioxide. The tubes usually exhibited internal pressure when they were opened. The tubes were allowed to stand some time at room temperature, during which time gas was liberated from the liquid.

The reaction mixture (38 g) was separated by distillation into 3 fractions: the first fraction (9 g) with a b.p. of 43-46° at atmospheric pressure was allyl chloride (b.p. = 46°, according to Tollens); the second fraction (4 g) with a b.p. of 46-69° (27 mm) was mainly 1,2,3-trichloropropane; and the third fraction was 18.4 g of 1,2,3-dichloronitropropane, with a b.p. of 96-105° (at 13 mm). About 2 g of a liquid, apparently allyl chloride, was collected in a trap connected into the vacuum line behind the collecting vessels and chilled with acetone and carbon dioxide. As a rule, some 0.5 g of tarry residue remained in the distilling flask.

Distillation without vacuum of the 46-69° (27 mm) fraction yielded 1,2,3-trichloropropane with a b.p. of 156° (b.p. = 158° according to Carius, $d_4^{15} = 1.4206$; according to Lineman, $d_4^{15} = 1.417$) with a yield of about 25% of the theoretical.

Second distillation of the 96-105° (13 mm) fraction yielded 15 g of 1,2-dichloro-3-nitropropane with a b.p. of 94.5° (at 8 mm). The yield of nitrosyl chloride was 55% of the theoretical.

5.910 mg, 7.800 mg substance: 4.840 mg, 6.370 mg CO_2 ; 1.620 mg, 2.360 mg H_2O .
5.901 mg, 7.350 mg substance: 0.452 ml, 0.5615 ml N_2 (24°, 748 mm).
14.015 mg, 12.590 mg substance: 8.818 ml 7.843 ml 0.02 N $AgNO_3$.
0.1786 g substance: 30 g benzene: At 0.1966°.
Found %: C 22.33, 22.26; H 3.07, 3.77; N 8.82, 8.57;
Cl 44.52, 44.18; M 155.0.
 $C_3H_5ONCl_2$. Calculated %: C 22.75; H 3.16; N 8.87; Cl 44.93; M 158.0.

1,2-dichloro-3-nitropropane is a colorless oily liquid with a sharp odor, which turns pale yellow upon standing; d_4^{20} 1.4597; n_D^{20} 1.4762. The substance is insoluble in water and is miscible with the usual organic solvents.

When the substance is shaken up with a 10% aqueous solution of caustic soda at room temperature, it dissolves, turning the solution orange-yellow. When the alkaline solution is treated with sodium nitrite and sulfuric acid, we get the usual nitrolic reaction of the primary nitro group. The pseudo-nitrole reaction for the secondary group is negative.

The substance dissolves when boiled with hydrochloric acid, forming hydroxylamine and 1,2-dichloropropionic acid.

5 g of dichloronitropropane and 20 ml of hydrochloric acid (sp. gr. 1.18) were boiled together for 2.5 hours with a reflux condenser. The cooled solution was extracted with ether, and the extract dried with sodium sulfate. 2.3 g of hydroxylamine hydrochloride was isolated with 100% yield from the hydrochloric-acid solution after it had been evaporated to dryness over a water bath. The salt, recrystallized from alcohol, fuses at 152° (the melting point of hydroxylamine hydrochloride is 151° according to the tables), and exhibits all the hydroxylamine reactions. A test sample consisting of a mixture of the substance with hydroxylamine hydrochloride exhibited no depression of the melting point.

When an ether extract of the residue (2.4 g) is distilled, after the ether has been driven off, we succeeded in isolating about 1 g of a substance with a b.p. of 124-126° (25 mm), which is not wholly pure 1,2-dichloropropionic acid (b.p. = 210° at atmospheric pressure, according to Henry). The substance possesses the characteristic odor of an organic acid, is soluble in water, and is titrated with caustic soda in the presence of phenolphthalein. Titration gave the acid content as about 97%.

6.040 mg, 5.460 mg substance; 5.954 mg, 5.157 mg CO₂; 1.916 mg, 1.760 mg H₂O.
Found %: C 25.25, 25.75; H 3.58, 3.60.
C3H4O2Cl2. Calculated %: C 25.17 H 2.80.

Somewhat lower results were obtained in determining the chlorine, probably because of the presence of impurities in the form of saponification products of dichloro-propionic acid in the substance.

3. Condensation of Allyl Chloride with Nitrosyl Chloride

Preparation of 1,1-Dichloro-2-nitroethane

(Experimental Work Done by V. Y. Pilskaya)

A mixture of 70 g of vinyl chloride and 70 g of nitrosyl chloride (molar proportions) was allowed to stand at room temperature for six days in sealed tubes. The reaction is complete before that time, however.

After the tubes had been opened and the gaseous products removed, there remained 76 g of a blue liquid that fumed in air. When this was distilled in vacuum, 27 g of trichloroethane, slightly colored with traces of the nitroso compound, distilled over at 40-45° (80 mm). (Redistillation of the distillate

at ordinary pressure yielded a substance with a b.p. of 113.5-114° (at 7.56 mm), d_{20}^{20} 1.551, n_D^{20} 1.635., which are the constants of trichloroethane.)

The second fraction passed over as 15 g of a yellowish liquid with a b.p. of 45-48° (5 mm), which proved to be dichloronitroethane; the yield was 20% of the theoretical. Then there passed over a substance that congealed as white crystals (8 g), which was identified by its melting point (61-62°) and other properties as chloroacetic acid. The residue consisted of 26 g of a brown, undistillable tar.

Pure 1,1-dichloro-2-nitroethane is a liquid that is pale yellow, with a b.p. of 45-46° (5 mm) and a d_{15}^{15} 1.4900; n_D^{15} 1.4765. The substance is soluble in the usual organic solvents.

0.1880 g substance: 0.117 g CO_2 ; 0.030 g H_2O .

4.538 mg substance: 0.33 ml N_2 (20°, 751 mm).

0.1400 g substance: 0.2755 g AgCl .

Found %: C 16.27; H 1.78; N 10.47; Cl 49.39.

$\text{C}_2\text{H}_3\text{O}_2\text{NCl}_2$. Calculated %: C 16.67; H 2.08; N 9.73; Cl 49.28.

The substance exhibits all the properties of a primary nitroparaffin; upon saponification with concentrated sulfuric acid it yields dichloroacetic acid.

6 g of dichloronitroethane and 10 g of 96% sulfuric acid were placed in a flask fitted with a reflux condenser. The mixture was strongly heated for a few minutes, after which heating was continued over a water bath. The reaction products were distilled from the mixture in vacuum, 6 g of a colorless liquid - dichloroacetic acid (80% of the theoretical) passing over at 86-93° (10 mm). A substance with a b.p. of 192-193° was isolated by a second distillation.

0.1298 g substance: 20.36 ml 0.1 N AgNO_3 .

Found %: Cl 55.62.

$\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2$. Calculated %: Cl 55.36

4. Condensation of Vinylidene Chloride with Nitrosyl Chloride

Preparation of 1,1-dichloro-2-nitroethylidene $\text{Cl}_2\text{C}=\text{CHNO}_2$

A mixture of 30.0 g of vinylidene chloride (b.p. = 30.5-34°) and 21.0 g of nitrosyl chloride was sealed into 3 ampoules (about 1.7 g of the mixture being placed in each ampoule). After standing for 48 hours at room temperature, the color of the reaction mixture changed from dark red to light green. A day later a small crystalline precipitate appeared in the tubes. When the chilled tubes were opened, internal pressure was found to exist, and an appreciable quantity of hydrogen chloride was liberated. After the gaseous reaction products had been eliminated by warming the reaction mass up to room temperature, the mixture, totalling 41.5 g, was subjected to distillation. After the excess vinylidene chloride had been driven off at atmospheric pressure, 23.0 g of a 80-124° fraction distilled over (the bulk - 18.2 g - distilled over at 115-124°). The residue (8 g) left after the first fraction had distilled over was then distilled in vacuum; 5.0 g of a substance with a b.p. of 65-68.5° at 27 mm was obtained. The residue in the distilling flask (2.0 g) was a viscous tarry mass, consisting, most probably, of the products of the

polymerization of the vinylidene chloride. A large part of a sample (35% by weight) of the first fraction (80-124° at atmospheric pressure) entered into solution when it was treated with a 2% solution of caustic soda, coloring the solution orange-yellow, which is characteristic of solutions of the salts of acinitro compounds. Efforts to isolate a nitro product from this reaction by fractionating it were fruitless, however. When that part of the liquid that passed over at 115-124° was redistilled with a dephlegmator, it passed over as an indivisible mixture with a b.p. of 115-118° (probably azeotropic). To eliminate the nitro product, 9.5 g of this mixture was shaken up with a 2% solution of caustic soda. After two washings (the alkali was no longer discolored), the mobile oil (6.0 g) was washed with water, dried, and distilled; all the substance passed over at 124-129.5°. Most of the substance boiled at 128-129°; it proved to be pure asymmetrical tetrachloroethane, d_4^{20} 1.5446, n_D^{20} 1.4873 (according to Stadel the b.p. of asymmetrical tetrachloroethane is 129-130° with d_6^{25} 1.5424).

A pure substance with a b.p. of 58.5° (12 mm), which proved to be 1,1-dichloro-2-nitroethylene, was isolated from the product with a b.p. of 65-68.5° at 27 mm.

Nitrodichloroethylene is a mobile oil, with a slightly yellow color, and a d_4^{20} 1.5652, n_D^{20} 1.5172. The substance is slightly soluble in water, and dissolves under ordinary conditions when shaken up with a 10% aqueous solution of caustic soda, turning it orange-yellow. It does not exhibit the pseudonitrolic reaction of a secondary nitro group. It rapidly bleaches a neutral aqueous permanganate solution at room temperature.

The yield (greatly reduced because of the loss of 8 g of the nitro product as tetrachloroethane) is 25% of the theoretical in terms of nitrosyl chloride.

0.1012 g substance; 20 g benzene: At 0.187°.
4.703 mg, 2.987 mg substance: 0.4212 ml, 0.2548 ml N_2 (17°, 736 mm).
12.720 mg, 11.080 mg substance: 8.757 ml, 7.631 ml 0.02 N $AgNO_3$.
Found %: N 9.96, 9.64; Cl 48.82, 48.85; M 138.5
 $C_2HO_2NCl_2$. Calculated %: N 9.82; Cl 49.50; M 142.

5. Condensation of Trichloroethylene with Nitrosyl Chloride

Preparation of 1,1,2,2-Tetrachloro-2-Nitroethane

20 g of trichloroethylene (b.p. 85°) and 10 g of nitrosyl chloride (molar proportions) were placed in each of two tubes, which were then sealed; the sealed tubes were set aside to stand at room temperature for 14 days. No noticeable change in color was observed during this interval. When the tubes, which had been chilled in acetone and carbon dioxide, were opened, an internal pressure was observed. After the unreacted nitrosyl chloride had been driven off, we obtained a dirty-green residue (55.0 g) which turned colorless upon further heating. The residue was broken down into three fractions by distillation.

The first fraction (37.0 g) passed over at atmospheric pressure at 82-85°, and turned out to be trichloroethylene. The residue of 9.5 g left behind after the trichloroethylene had been driven off was distilled in

vacuum; 2.2 g of a mixture boiling at 46-62° (9 mm) and 3.8 g of a substance with a b.p. of 64-66.5° (9 mm) was collected. 2.0 g of liquid was collected in a trap along the vacuum line that was chilled with an acetone-carbon dioxide mixture. The residue in the distilling flask (0.5 g) was a dark, tarry mass.

A compound with a b.p. of 55-56° (17 mm), identified by its b.p. of 158° at atmospheric pressure, its density of d_4^{20} 1.6834 and its index of refraction of n_D^{25} 1.49 as pentachloroethane, was isolated by repeated redistillation from the 46-62° (9 mm) fraction, collected from several runs. (The corresponding constants for pentachloroethane are: b.p. 159°, d_4^{25} 1.6712, and n_D^{25} 1.49, according to Beilstein). The yield is 50% of the theoretical in terms of the initial trichloroethylene).

3.6 g of 1,1,2,2-tetrachloro-2-nitroethane with a b.p. of 63° (8 mm) was isolated after repeated redistillation from the 64-66.5° (9 mm) fraction. A small amount (about 0.5 g) of the same substance was isolated from the distillation residue left after redistillation of the 46-62° (9 mm) fraction. The yield was 88% in terms of the initial trichloroethylene.

5.39 mg, 4.10 mg substance: 2.039 mg, 1.649 mg CO_2 ; 0.520 mg, 0.320 mg H_2O .

7.900 mg substance: 0.4459 ml N_2 (14.5°, 755 mm).

5.428 g substance: 0.2901 ml N_2 (21°, 763 mm).

0.2669 g, 0.1600 g substance: 52.3 ml, 30.94 ml 0.1 N AgNO_3 .

0.2309 g substance: 20 g benzene : At 0.284°.

Found %: C 10.83, 10.59; H 0.86, 1.08; N 6.31, 6.22.
Cl 68.57, 69.48; M 208.1

$\text{C}_2\text{HO}_2\text{NCl}_4$. Calculated %: C 11.20; H 0.47; N 6.57; Cl 66.6; M 213

Tetrachloronitroethane is an oily substance, slightly yellowish in color, that is insoluble in water and miscible with the usual organic solvents.

The substance does not dissolve when shaken up for a long time at room temperature with a 40% aqueous solution of caustic soda. It dissolves when boiled with alkalis, decomposing. When a drop of the substance is heated in a test tube over the open flame of a burner, it breaks down, liberating nitrogen oxides and manifesting the odor of an acid halide. A strip of paper wetted with dimethylaniline turns a characteristic bright yellow when exposed to vapor of the substance at room temperature, subsequently turning lemon-yellow in the air.

SUMMARY

1. The reactions of nitrosyl chloride with isobutylene, allyl chloride, vinyl chloride, vinylidene chloride, and trichloroethylene were investigated. The products obtained were: the dimer of the oxime of chloro-isobutyraldehyde; 1,2-dichloro-3-nitropropane; 1,1-dichloro-2-nitroethane; 1,1-dichloro-2-nitroethylene; and 1,1,2,2-tetrachloro-2-nitroethane.

2. It was shown that in most cases the addition of nitrosyl chloride depends upon the polarity of the reacting ethylene and N—Cl bonds, the negative halogen attaching itself to the positive carbon atom, and the positive nitroso group attaching itself to the negative carbon atom.

3. The structure of nitrosyl chloride and the influence of halogen substituents upon the nitroso-oxime rearrangement are considered.

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INVESTIGATION OF THE PROCESS FOR THE PRODUCTION OF
THE METHYL AND ETHYL ESTERS OF ORTHOSILICIC ACID

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The esters of orthosilicic acid were first synthesized in 1844. Since that time various methods have been proposed for their preparation [1].

At the present time the generally accepted method of synthesizing the esters of orthosilicic acid is the reaction of absolute alcohol with silicon tetrachloride. But in the synthesis of the methyl ester of ortho silicic acid, the dimethyl-diallyl silicate, etc., by this method the yields of the indicated esters was very low.

Engaged for a long time in the preparation of the esters of orthosilicic acid and the thorough investigation of the processes therein involved, we elucidated the reasons for the low yields of the reaction end products, and we developed a perfected method for the synthesis of the simplest esters of orthosilicic acid.

As our investigations have demonstrated, the processes that take place during the synthesis of the alkoxy silanes are rather complex and are accompanied by a number of side reactions.

In our investigation of the products of the interaction of silicon tetrachloride with these alcohols we established the fact that, in addition to the esters of orthosilicic acid, alkoxychloro-silanes, halogen derivatives, simple ethers, hydrogen chloride, and the condensation products of the alkoxy silanes are formed.

The formation of these products may be attributed to the following processes:

- 1) $\text{ROH} + \text{SiCl}_4 \rightarrow \text{ROSiCl}_3 + \text{HCl}$,
- 2) $\text{ROH} + \text{ROSiCl}_3 \rightarrow (\text{RO})_2\text{SiCl}_2 + \text{HCl}$,
- 3) $\text{ROH} + (\text{RO})_2\text{SiCl}_2 \rightarrow (\text{RO})_3\text{SiCl} + \text{HCl}$,
- 4) $\text{ROH} + (\text{RO})_3\text{SiCl} \rightarrow (\text{RO})_4\text{Si} + \text{HCl}$,
- 5) $2\text{ROH} \xrightarrow[-\text{H}_2\text{O}]{\text{SiCl}_4} \text{ROR}$.

The hydrogen chloride formed in these reactions reacts in turn with the

alcohols, resulting in the formation of chlorine derivatives:



The water that is contained in the insufficiently dehydrated alcohol or formed in the course of the side reactions results in the formation of hydroxy silane compounds:

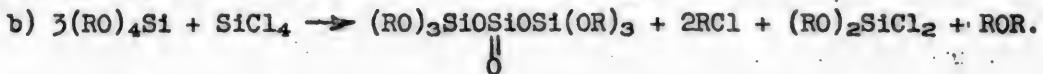


The hydroxy compounds formed undergo subsequent condensation, accompanied by the formation of polymer compounds:



When much water is present, the silicon tetrachloride and the products of the reaction with the alcohols are completely hydrolytically cleaved, resulting in the formation of polysilicic acids.

The excess silicon tetrachloride, which is very often employed in the preparation of complete esters of orthosilicic acid, is harmful. When the esters of orthosilicic acid are heated with silicon tetrachloride, the alkoxychlorosilanes (a) are formed, as well as simple ethers, halogen derivatives, and polymerized compounds (b):



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Thus, the lowered yields of esters is due to the following reasons:

- 1) Side processes, resulting from different directions of the reaction of silicon tetrachloride with alcohols, accompanied by the formation of alkoxy-chlorosilanes;
- 2) The formation of halogen derivatives, constituting gaseous products (CH_3Cl b.p. = -23.7° ; C_2H_5Cl b.p. = $+13^\circ$) that easily escape during the reaction, when methyl and ethyl alcohols are employed;
- 3) Condensation of the products of the hydrolytic cleavage of the alkoxy- and halogen silanes, resulting in the formation of high-boiling polymer products;
- 4) Reaction of the excess silicon tetrachloride with the esters of silicic acid, accompanied by the formation of alkoxy-chlorosilanes, chlorine derivatives, ethers, etc.;
- 5) Losses of the reaction products owing to evaporation, caused by the evolution of heat in the reaction mass, to the exothermic nature of the process, or the recommended artificial heating at the end of the synthesis;
- 6) Formation of multicomponents, which pass over together with the mixtures consisting of alcohols, ethers, alkoxy-silanes, chlorine compounds, etc.

The method for the preparation of the esters of orthosilicic acid suggested by us is founded upon the following principles that have justified themselves in practice:

- 1) Carrying out the process with the reaction mixture chilled by strong freezing mixtures;

2) Removing the hydrogen chloride formed by blowing chilled dry air through the reaction mass.

3) Introducing the silicon tetrachloride into the alcohol by feeding it through a capillary tube extending down to the bottom of the reaction flask instead of dropping it from a dropping funnel;

4) Chilling the reaction mixture to prevent the stage of subsequent heating.

EXPERIMENTAL

The initial substances for the synthesis of the esters of orthosilicic acid used by us were methyl alcohol (b.p. 65°, sp. gr. 0.790) and ethyl alcohol (b.p. 78°, sp. gr. 0.789), dehydrated with metallic sodium, and freshly prepared and repeatedly purified chemically pure silicon tetrachloride (b.p. 57°, sp. gr. 1.48).

The esters were prepared in a 500-ml three-necked flask. The flask was fitted with a reflux condenser, a dropping funnel with a tip drawn out into a capillary, a thermometer, and a capillary tube for passing chilled dried air through the mixture. The dehydrated alcohol was used in excess, on the basis of 4.4 moles per mole of silicon tetrachloride. First, the calculated quantity of methyl or ethyl alcohol was placed in the flask. The flask and its alcohol were then chilled with solid carbon dioxide. The silicon tetrachloride was introduced through the capillary that reached to the flask wall, which was chilled with solid carbon dioxide. The silicon tetrachloride was added at a rate of about 0.5 g per min. As the reaction proceeded, air that had been carefully dried over calcined calcium chloride and phosphorus anhydride and was free from carbon dioxide was blown through the reaction mixture to remove the hydrogen chloride formed. Throughout the process the contents of the flask were carefully stirred by means of a glass propeller agitator fastened to the wide neck of the flask and fitted with a hydraulic seal.

The flask was not heated after all the silicon tetrachloride had been added to the reaction mixture, as is usually recommended for the end of the synthesis, dry air continuing to be blown through the contents of the flask.

Test No.	Mean yield of ortho-silicic-acid esters attainable by usual method of synthesis (%)		Mean yield of ortho-silicic acid esters attainable by intense chilling of the flask contents (%)		Mean yield of ortho-silicic-acid esters attainable by the method here proposed (%)	
	Methyl alcohol	ethyl alcohol	Methyl alcohol	ethyl alcohol	methyl alcohol	ethyl alcohol
1	~ 40	60.7	61.5	74.0	67.4	79.4
2	~ 40	63.2	62.0	76.2	66.5	78.5
3	~ 40	61.0	60.8	77.8	68.1	80.0
Average	~ 40	61.6	61.4	76.0	67.3	79.3

The reacted mass was then poured into a Claisen flask and fractionated.

The yield of esters of orthosilicic acid obtained exceeded the yield obtainable by the usual method of synthesis by more than 10%, as is shown in the above Table.

The residue left in the flask after fractionation was a high-boiling fraction consisting of polymers of the esters of orthosilicic acid.

SUMMARY

1. It was found that the production of the esters of orthosilicic acid is accompanied by a number of side processes that lower the ester yield.
2. It was established that the losses of reaction products are caused by the unjustifiable prolonged heating of the reaction mixture after the silicon tetrachloride had been added.
3. A new method is suggested for the preparative production of alkoxy-silanes.

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RESEARCH IN THE CATALYTIC CONVERSION OF ALCOHOLS INTO
HYDROCARBONS OF THE DIVINYL SERIES

XIV. CATALYTIC TRANSFORMATION OF TERTIARY BUTYL ALCOHOL
AND ITS BINARY MIXTURES WITH METHYL ALCOHOL AND FORMALDEHYDE

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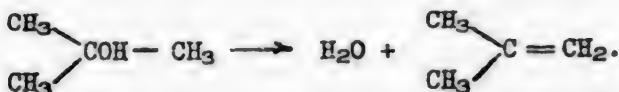
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In our previous papers we demonstrated the applicability of the S.V. Lebedev reaction [1] to the primary alcohols (propyl and butyl) [2] and the secondary alcohols (isopropyl and secondary butyl) [3] and the production from these alcohols of hydrocarbons with conjugated systems of double bonds, in which the number of carbon atoms was twice that of the initial alcohol.

At an earlier date we proved that the reaction involving the formation of diethylene hydrocarbons takes place via the dehydrogenation of the alcohols into the corresponding aldehydes or ketones (depending upon the alcohol used in the research), after which the carbonyl compound produced undergoes condensation, the condensation of the aldehydes being accompanied by the splitting off of water and resembling the conversion of acetaldehyde into crotonaldehyde, while that of the ketones is analogous to the conversion of acetaldehyde into mesityl oxide. Subsequently, the reaction products, which are unsaturated aldehydes or ketones, undergo reduction into the corresponding unsaturated alcohols, which are dehydrated under the influence of the water-splitting component of the catalyst, with a rearrangement of the bonds and the formation of a conjugated system [4]. Thus, the doubling of the molecules required for the formation of a diethylene hydrocarbon must take place via the condensation of carbonyl compounds.

It was of interest to explore the feasibility of producing diethylene hydrocarbons from tertiary alcohols catalytically. From the viewpoint of our theory, diethylenic hydrocarbons cannot be formed in the catalytic conversion of tertiary alcohols by the S.V. Lebedev reaction, as tertiary alcohols cannot shift to carbonyl compounds, through which the catalytic synthesis of diethylenic hydrocarbons is accomplished.

Our results in testing a tert. butyl alcohol (trimethylcarbinol), set forth in the present paper, confirmed this conclusion. Both with the modified S.V. Lebedev catalyst and with a single dehydrogenating component that possesses the same strong condensing properties [4], no condensation products were recovered at a temperature of 300-380°. In both instances the reaction product was isobutylene:



This excludes the possibility of condensation by means of intermolecular dehydration of two molecules of alcohol.



It was shown in our previous reports that under the influence of the S.V. Lebedev catalyst a mixed condensation and the formation of diethylenic hydrocarbons with conjugated bonds [5] occurs in binary mixtures of various alcohols or in a binary mixture of an alcohol and some carbonyl compound, aldehyde, or ketone. In particular, one of the authors, together with K. Charskaya, proved that divinyl is formed from a mixture of isopropyl and methyl alcohols, as well as from a mixture of isopropyl alcohol and formaldehyde [6].

It appeared to be of some interest to clear up the possibility of forming diethylenic hydrocarbons from binary mixtures of tert. butyl alcohol and some other alcohol or aldehyde, thus establishing the possibility of the participation of tert. butyl alcohol in the mixed condensation reaction. To this end we subjected mixtures of tert. butyl alcohol and methyl alcohol (1:2, 1:1 in mol ratios) and a mixture of tert. butyl alcohol and formaldehyde to contact conversion over catalysts consisting of mixtures of both components (dehydrogenating and dehydrating), taken in ratios of 98:2 and 95:5. The tests were run at 300 and 280°.

We ascertained that no diethylenic hydrocarbons were formed in any of the experiments undertaken, nor, for that matter, were there any noticeable amounts of any condensation products. Evidently, in this instance, there is no condensation reaction between a tertiary alcohol and formaldehyde, as it requires the formation of a carbonyl compound in an intermediate stage, whereas tertiary alcohols are unable to form carbonyl compounds, as has already been said.

Thus, these tests prove the absence of a direct condensation process between an alcohol and an aldehyde in accordance with the following reaction:



and, consequently, no diethylene hydrocarbons are formed (in the present case, we might expect the dehydration of the glycol to yield 2-methylbutadiene-1,3).

Our data likewise indicate that the equations of I.I. Ostromyslensky and A.A. Balandin [8] were not confirmed experimentally in their application to the present case.

EXPERIMENTAL

Tertiary butyl alcohol was prepared by the hydration of isobutylene via butylsulfuric acid. Saponification of the latter yields an aqueous solution of the alcohol. When the aqueous solution was fractionated, an azeotropic mixture with water was obtained with a b.p. of 80-80.5°; d_4^{20} 0.816, containing 88.24%

alcohol and 11.76% water [9]. In redistillation under the same conditions this product served as the initial materials for our research. The methanol was first dried with potash and distilled. B.p. 65.5-66.5°; d_4^{20} 0.793. The formaldehyde was produced by oxidizing methanol with a copper spiral. The oxidation products were collected in a receiver chilled with ice and filled with a known quantity of tertiary butyl alcohol. The solution of formaldehyde in tert. butyl alcohol thus prepared was used in our research. The formaldehyde concentration was determined with hydroxylamine. The amount of methanol or of water was not calculated.

The tests were made in a laboratory electric furnace with a reaction tube 1 m long and 30 mm in diameter; the heating zone was 70 cm long. Before the charge was placed in the tube, the catalyst was activated by heating to 500° in a muffle furnace for 2 hours. After the run the catalyst had to be regenerated at 500° in a current of air for 1 hour. In tests using tert. butyl alcohol alone, 100 ml of the alcohol was passed through the furnace at the rate of 1 ml per minute. In tests using mixtures, 60 ml of the mixture was passed through at the same rate. In tests using mixtures, the burette from which the mixture was fed to the furnace was closed by a rubber stopper containing a glass tube connected to a Tee reaction tube. Thus, the formaldehyde, part of which might evaporate from the mixture, was again fed into the reaction zone. The liquid reaction products (the condensate) were collected in a receiver chilled by ice, while the gas passed on to a gas tank, the sealing liquid of which was a saturated solution of sodium chloride.

The gaseous products were analyzed by the method, devised by A.F. Dobryansky, of absorbing unsaturated hydrocarbons in solutions of sulfuric acid of different concentrations. The hydrogen was determined by combustion over paladinized asbestos.

In tests using tert. butyl alcohol alone, the percentage of undecomposed alcohol in the condensate was determined by measuring the latter's specific gravity. To ascertain whether there were any water-insoluble compounds (hydrocarbons or higher alcohols), products of the condensation of the particles in the initial substances, in the liquid reaction products, the condensate was diluted with water. The test results are given in Tables 1 and 2. Table 1 shows that the principal reaction products of tert. butyl alcohol are gaseous unsaturated hydrocarbons, which prove to be isobutylene. The negligible quantity of hydrogen in the gas is due either to impurities that the initial product may have contained (which is improbable), or to a partial rearrangement, which the data in the literature indicate tert-butyl alcohol may undergo when acted upon by a dehydrogenating catalyst [10]. No oily layer separated out when the condensate was diluted with water. This indicates the absence of condensation products of trimethylcarbinol packing. Under these conditions the dehydrogenating component produces a comparatively shallow decomposition of the alcohol, but even in this case no condensation products were observed to form.

Table 2, listing the results of tests with mixtures of tert. butyl alcohol with methanol or formaldehyde, shows that the principal reaction products are the gaseous C₄ hydrocarbons, evidently isobutylene.

The gas from tests using mixtures of the alcohol and formaldehyde were analyzed in the Korotkov apparatus for the percentage of diethylenic hydrocarbons with conjugated bonds. Practically nothing was absorbed by the maleic anhydride.

Table 1
Catalytic Conversion of Tert- Butyl Alcohol

Catalyst	Temperature	Absolute alcohol passed through (g)	Output		Composition of gas % by vol.					d_4^{20} of condensate	Percent of unreacted acid	Yield of isobutylene (% by weight)	Condensation products
			ans (l)	Condensate (g)	H ₂	CO	CO ₂	C _n H _{2n}					
Modified S.D. Lebedev catalyst	300°	72	20.5	28.43	2.9	0.0	0.8	96.4	0.9937	99.1	69.0	none	none
	380°	72	20.7	28.08	3.4	0.0	0.0	95.3	0.9967	99.3	68.4	none	none
Dehydrogenating catalyst component.....	300°	72	2.6	75.15	6.6	0.0	1.1	92.2	0.8220	11.25	64.3	none	none
	380°	72	12.1	50.9	9.2	0.1	0.9	88.8	0.8710	56.9	65.5	none	none

Table 2
Catalytic Conversion of Binary Mixtures of Tert. Butyl Alcohol
With Methanol and Formaldehyde

Composition of alcohol mixtures, moles	Catalyst	Temperature	Amount of mixture passed through(g)	Composition of gas % by vol.					H_2
				Gas evolved, liters NTP	CO ₂	Absorbed by 83% H ₂ SO ₄ (C ₄ H ₆ +C ₂ H ₆)	Absorbed by 100% H ₂ SO ₄ (C ₂ H ₄)		
Tert-butyl + methyl 1:1	{ 95/5 98/2	380°	51.3	12.5	4.8	74.5	1.0	15.8	
		300	50.1	12.7	1.5	77.4	0.8	16.2	
Ditto 1:2	{ 98/2 98/2	380	47.2	9.9	2.0	65.1	1.3	16.5	
		300	47.6	6.6	0.8	80.7	3.8	8.3	
Tert-butyl + formaldehyde 1:0.7	98/2	380	89.9	15.5	3.1	76.3	1.9	7.7	
Ditto 1:1.7	93/2	380	97.5	13.3	5.8	55.4	2.0	22.8	

NOTE: The numerator of the catalyst column denotes the percentage of the dehydrogenation component, the denominator, the percentage of the dehydrating component.

In tests using mixtures of alcohols, the liquid was seen to grow cloudy when the condensate was diluted with water, but no hydrocarbon layer separated out. Only in tests using mixtures that contained formaldehyde were individual drops of oil found, but in negligible quantity. The formation of these drops should be ascribed to the condensation of the formaldehyde itself.

SUMMARY

1. The contact conversion of tert. butyl alcohol over the dehydrogenating component of a catalyst and over a modified S.V.Lebedev was investigated at 300 and 380°.
2. It was shown that under these conditions no higher alcohols or hydrocarbons are formed as condensation products.
3. The catalytic conversion of binary mixtures of tert. butyl alcohol with methanol or formaldehyde over mixed S.V.Lebedev catalysts with 95/5 and 98/2 component ratios at 300 and 380° was investigated. It was found that no complex products of the mixed condensation of tert. butyl alcohol and formaldehyde are formed.

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THE REACTION OF ETHYLENEDIAMINE WITH ORGANIC ACIDS

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Ethylenediamine can enter into complex formations with salts of inorganic and organic acids. Complex compounds of ethylenediamine with succinic, formic, maleic, thiocyanic, laevomaleic, and dextro tartaric acids of the following composition have been synthesized and described in the literature:[1]:
 $C_2H_4(NH_2)_2 \cdot C_4H_6O_4$, $C_2H_4(NH_2)_2 \cdot C_4H_4O_4$, $C_2H_4(NH_2)_2 \cdot \underline{C}_4H_6O_5$, $C_2H_4(NH_2)_2 \cdot \underline{d}C_4H_6O_6$,
 $C_2H_4(NH_2)_2 \cdot 2\underline{d}C_4H_6O_6$ and $C_2H_4(NH_2)_2 \cdot 2HCNS$.

It is evident from this list that ethylenediamine forms compounds with a 1:2 ethylenediamine-acid ratio with monobasic acids and with a 1:1 ratio with dibasic acids, with the sole exception of d-tartaric acid, with which ethylene forms two compounds, with 1:1 and 1:2 ratios. To supplement the rather sparse material in the literature the reaction of ethylenediamine with benzoic, salicylic, maleic, and phthalic acids and with maleic anhydride was investigated.

The research was done by the visual polythermal method of physical-chemical analysis [2], which makes it possible to find from "composition-property" diagrams the chemical action between components without preparatively isolating the compounds synthesized. The quantitative measurement of the "composition-property" chemical diagrams reveals the existence of special phase types, providing the researcher with valuable criteria for judging the nature of a compound.

EXPERIMENTAL

The Ethylenediamine - Benzoic Acid System

The ethylenediamine was refined by distillation over metallic sodium. The results of the investigation of the binary system ethylenediamine - benzoic acid are given in Table 1 and Fig. 1.

As may be seen from Table 1 and Fig. 1, as more and more benzoic acid is added to the ethylenediamine, the temperature at which the initial crystals separate out drops, reaching the eutectic point C_1 , with a m.p. of -23° , corresponding to 74 mol.% of ethylenediamine and 26 mol.% of benzoic acid. Then, as more benzoic acid is added to the mixture, the temperature of deposition of the initial crystals rises sharply, reaching a maximum at 33.33 mol.% of

Table 1

Test No.	Mol. %		Temperature	
	$C_2H_4(NH_2)_2$	C_6H_5COOH	Deposition of first crystals	Crystallization of the eutectic
1	100	0	8.5°	
2	98	2	-3	
3	95	5	-7	
4	90	10	-10	
5	85	15	-13	
6	75	25	-22	-23
7	74	26	-23	-23
8	68.5	31.5	-18	
9	55.9	44.1	20	
10	52.1	47.9	48	
11	50	50	89	
12	40	60	120	
13	33.33	67.66	135	
14	25	75	125	
15	20	80	90	90
16	10	90	105	90
17	8	92	113	
18	6	94	119	
19	0	100	121.4	

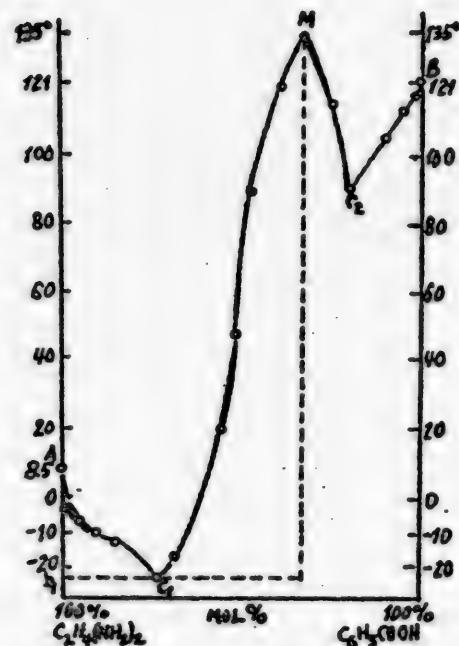


Fig. 1

ethylenediamine and 66.67 mol. % of benzoic acid. At this point a compound of ethylenediamine and benzoic acid, with the formula $C_2H_4(NH_2)_2 \cdot 2C_6H_5COOH$ and a m.p. of 135° is formed, the ethylenediamine - benzoic acid ratio being 1:2. This example confirms what has been asserted on the basis of previous investigations: that ethylenediamine forms molecular compounds with monobasic acids, such as thiocyanic acid, with a 1:2 ethylenediamine - acid ratio, even when the acid belongs to the aromatic series, such as benzoic acid.

The Ethylenediamine - Salicylic Acid System

The salicylic acid was purified by recrystallizing from hot water. The results of the research on this system are listed in Table 2 and Fig. 2.

As may be seen from Table 2 and Fig. 2, the curve of this system has two eutectics and one maximum. The first eutectic point, at -20°, corresponds to 87 mol. % of ethylenediamine and 13 mol. % of salicylic acid, and the second eutectic point, at 37°, corresponds to 40 mol. % of ethylenediamine and 60 mol. % of salicylic acid. The maximum, at 50°, corresponds to 50 mol. % of ethylenediamine and 50 mol. % of salicylic acid. Thus, ethylenediamine forms a single compound with salicylic acid, in a 1:1 ratio, the formula for which is $C_2H_4(NH_2)_2 \cdot C_6H_4(OH)COOH$, the melting point for this compound being higher than the melting point of ethylenediamine and lower than the melting point of salicylic acid. The phenol group in salicylic acid exhibits acid properties, whereas salicylic acid itself reacts like a dibasic acid with ethylenediamine.

Table. 2.

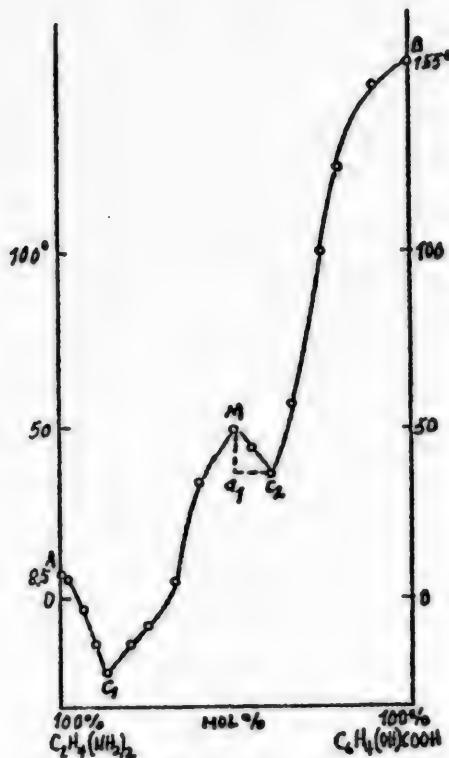


Fig. 2

Test No.	Mol. %		Temperature	
	C ₂ H ₄ (NH ₂) ₂	C ₆ H ₄ (OH)COOH	Deposition of first crystals	Crystallization of the eutectic
1	100	0	8.5°	
2	98	2	7	
3	94	6	-2	
4	90	10	-12	
5	87	13	-20	
6	80	20	-11	
7	75	25	-7	
8	66.7	33.3	6	
9	60	40	35	
10	50	50	50	
11	45	55	44	
12	40	60	37	
13	33.3	66.7	58	37
14	25	75	102	
15	20	80	127	
16	10	90	150	
17	0	100	156.5	

The Ethylenediamine - Maleic Acid System

The maleic acid was purified by recrystallization from water. The results of research on this system are given in Table 3 and Fig. 3.

The diagram of this system has two eutectic points. The first eutectic point, at 4°, corresponds to 90 mol.% of ethylenediamine and 10 mol.% of maleic acid. The second eutectic point, at 90°, corresponds to 15 mol.% of ethylenediamine and 85 mol.% of maleic acid. The maximum, at 148°, corresponds to 50 mol.% of ethylenediamine and 50 mol.% of maleic acid. The compound formed at this point has the formula $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2 \cdot \text{COOH}\text{C}_2\text{H}_2\text{COOH}$ and an ethylenediamine - maleic acid ratio of 1:1.

It was discovered during the investigation of this system that the system has a nonuniform viscosity that is a function of the component ratio. Beginning at a concentration of 90 mol.% of ethylenediamine and 10 mol.% of maleic acid in the system, the viscosity rises and an agreeable odor is noticed. The latter property reaches a maximum at a 1:1 ratio between the components. This leads to the conclusion that the ethylenediamine - maleic acid compound has a pleasant flowery odor and could be utilized in perfumery. At the points where the percentages of ethylenediamine and maleic acid are, respectively, as 80:20, 75:25 and 45:55, the system is highly viscous, and it took several days for the crystals to settle out at these points; that is why the temperature of disappearance of the last crystals was measured at these points.

Table 3

Test No.	Mol. %		Temperature	
	$C_2H_4(NH_2)_2$	$C_2H_2(COOH)_2$	Deposi- tion of first crystals	Crystal- lization of the eutectic
1	100	0	8.5°	
2	97	3	7	
3	94	6	6	
4	90	10	4	4°
5	87	13	26	
6	80	20	80	
7	75	25	106	
8	66.7	33.3	130	
9	60	40	138	
10	50	50	148	
11	45	55	143	
12	40	60	138	
13	33.3	66.7	120	
14	25	75	109	
15	20	80	100	
16	15	85	90	
17	10	90	102	90
18	5	95	116	
19	3	97	120	
20	0	100	130	

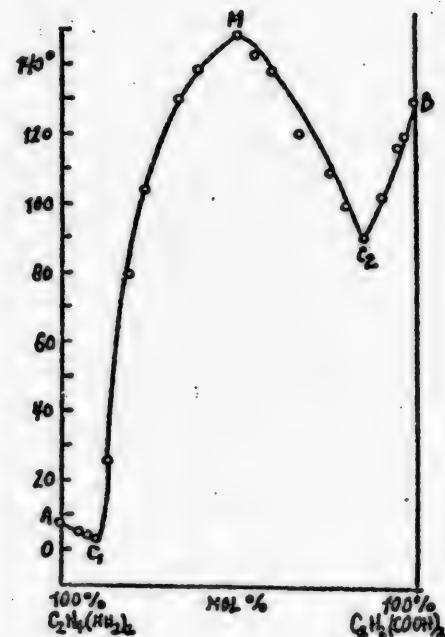


Fig. 3

The Ethylenediamine - Maleic Anhydride System

The results of research on this system are given in Table 4 and Fig. 4.

The formation of a chemical compound of ethylenediamine and maleic anhydride may be visibly followed from the outside, as the addition of suitable weighed batches of ethylenediamine to the maleic anhydride causes considerable heating of the test tube and a change of color. The colorless solution turns reddish, and the system's viscosity rises. As is seen in Table 4 and Fig. 4, the structural diagram of the ethylenediamine - maleic anhydride system has three eutectic points and two maxima. The first eutectic point C_1 , at 4°, corresponds to 98 mol.% of ethylenediamine and 2 mol.% of maleic anhydride; the second eutectic point C_2 , at 122°, corresponds to 40 mol.% of ethylenediamine and 60 mol.% of maleic anhydride; and the third eutectic point C_3 , at 52°, corresponds to 2 mol.% of ethylenediamine and 98 mol.% of maleic anhydride. The diagram has two maxima M_1 and M_2 , i.e., the reaction between ethylenediamine and maleic anhydride leads to the formation of two chemical compounds. The maximum M_1 , at 127°, corresponds to 33.33 mol.% of ethylenediamine and 66.67 mol.% of maleic anhydride. The maximum M_2 , at 196°, corresponds to 50 mol.% of ethylenediamine and 50 mol.% of maleic anhydride. The composition of these compounds is given by the following formulas:

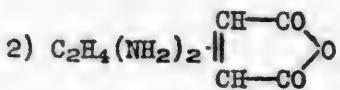
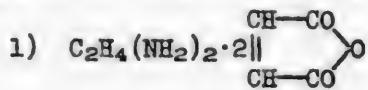


Table 4

Test No.	Mol. %		Temperature	
	$\text{C}_2\text{H}_4(\text{NH}_2)_2$	$\text{CH}-\text{CO}$ --- $\text{CH}-\text{CO}$ O	Deposition of first crystals	Crystallization of the eutectic
1	.100	0	8.5	
2	98	2	4	
3	95	5	45	
4	85	15	55	
5	75	25	75	
6	66.7	33.3	135	
7	60	40	152	
8	50	50	196	
9	40	60	122	
10	33.3	66.7	127	
11	30	70	117	
12	20	80	83	
13	10	90	57	
14	2	98	52	52
15	0	100	56.5	

The compounds do not dissociate upon fusion. The system forms a singular maximum at the point where the compound with a 1:1 ratio of the components is formed.

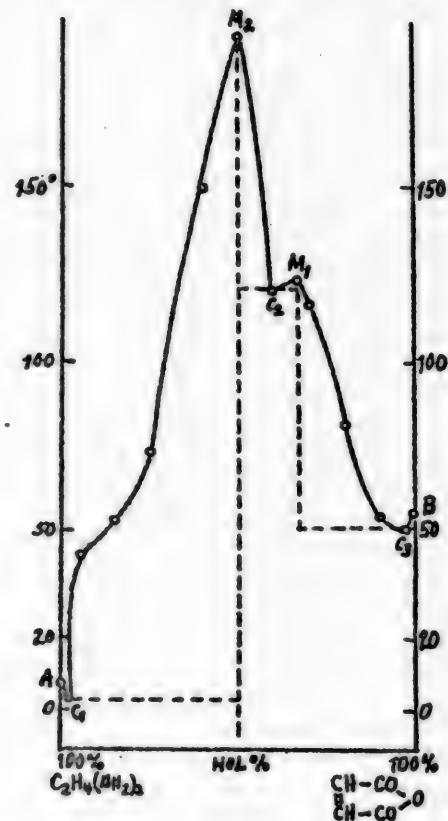


Fig. 4

The Ethylenediamine - o-Phthalic Acid System

The results of research on this system are listed in Table 5 and Fig. 5.

As is seen in Table 5 and Fig. 5, the structural diagram of the ethylenediamine - ortho phthalic acid system has three eutectic points. The first eutectic point C_1 , at -2° , corresponds to 92 mol.% of ethylenediamine and 8 mol.% of ortho phthalic acid; the second eutectic point C_2 , at 168° , corresponds to 52 mol.% of ethylenediamine and 48 mol.% of the phthalic acid; and the third eutectic point C_3 , at 137° , corresponds to 12 mol.% of ethylenediamine and 88 mol.% of the phthalic acid. The diagram has two maxima. The first maximum M_1 , at 212° , corresponds to 66.67 mol.% of ethylenediamine and 33.33 mol.% of phthalic acid. The second maximum M_2 , at 232° , corresponds to 33.33 mol.% of ethylenediamine and 66.67 mol.% of phthalic acid. The formula for the first compound is:



and for the second



It is held [3] that dibasic acids react with diamines in such a way that there is a free carboxyl group at one end of the elongated molecule and a free amino group at the other. This view is correct for compounds of ethylenediamine

Table 5

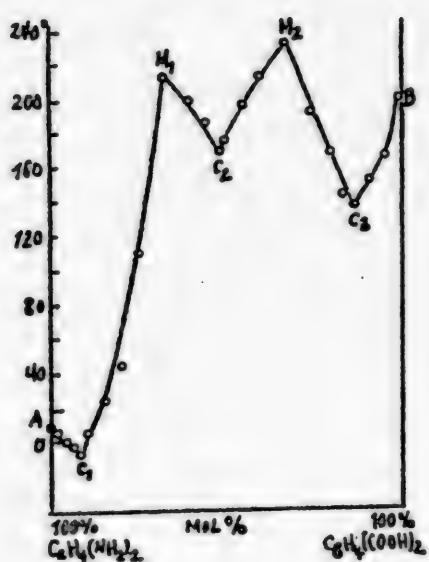


Fig. 5

and maleic acid. Phthalic acid reacts with ethylenediamine in such a way that when excess ethylenediamine is present, the amino groups of each end of the molecule remain free, whereas when the phthalic acid is present

in excess, the carboxyl groups are free. This reflects the influence of the aromatic ring of phthalic acid. A great increase in viscosity was noted in our investigation of this system, beginning at 85 mol.% of ethylenediamine in the mixture and 15 mol.% of phthalic acid. The viscosity reached a maximum at the dys-tectic point M_1 , at which crystallization lasted several days owing to the high viscosity of the solution. The melting point of this compound was measured in a special test tube. As the percentage of phthalic acid increases in the melts, the viscosity drops appreciably, the melt acquiring normal viscosity at a 1:1 ratio of the components in the system. Polyamide resins, synthesized from dibasic organic acids and diamines, amino acids, and analogous compounds, have been applied industrially as a result of the scientific and research work [3] of Carruthers and his pupils. The principal components of these resins are adipic and sebacic acids, and penta-, hexa- and decamethylenediamines.

These products were first employed in the production of the synthetic fiber known as "Nylon". Somewhat later the polyamides began to be worked by casting under pressure and pressing. When ethylenediamine is reacted with muconic acid, we get a resin with a m.p. of 61° . Research on the ethylenediamine-maleic acid

Test No.	Mol. % $C_2H_4(NH_2)_2$	Mol. % $C_6H_4(COOH)_2$	Temperature of deposition of first crystals	Crystallization of the eutectic
1	100	0	0.5°	
2	98	2	4	
3	96	4	1	
4	94	6	-1	
5	92	8	-2	
6	90	10	6	
7	85	15	23	
8	80	20	46	
9	75	25	110	
10	66.7	33.3	212	
11	60	40	198	
12	55	45	185	
13	52	48	168	168
14	50	50	175	
15	45	55	194	
16	40	60	212	
17	35.3	66.7	232	
18	25	75	191	
19	20	80	165	
20	15	85	142	
21	12	88	137	137
22	8	92	150	138
23	4	96	163	
24	0	100	197	

and ethylenediamine - phthalic acid systems by the visual thermal method has indicated that ethylenediamine forms viscous melts with these acids, which can yield resins whose melting points vary with the proportion of the component reagents, and hence, can be employed in the production of plastics.

N. B. Dolinina participated in this research.

SUMMARY

1. Binary systems formed from ethylenediamine and representatives of monobasic aromatic acids, aromatic phenol acids, unsaturated dibasic acids of the aliphatic series and dibasic acids of the aromatic series were investigated.
2. Ethylenediamine forms a compound with the formula $C_2H_4(NH_2)_2 \cdot 2C_6H_5COOH$ with benzoic acid, which has a m.p. of 135° .
3. With salicylic acid, ethylenediamine forms a compound $C_2H_4(NH_2)_2 \cdot C_6H_4(OH)COOH$, with a m.p. of 50° .
4. With maleic acid, ethylenediamine forms a compound $NH_2C_2H_4NH_2 \cdot COOHC_2H_2COOH$, which has an agreeable odor and a m.p. of 148° .
5. With maleic anhydride, ethylenediamine forms two compounds. The first compound with a 1:2 ethylenediamine - maleic anhydride ratio, has a m.p. of 127° , and the second, with a 1:1 ethylenediamine - maleic anhydride ratio, has a m.p. of 196° .
6. Ethylenediamine forms two compounds with ortho phthalic acid. One compound, $NH_2C_2H_4NH_2 \cdot COOHC_6H_4COOH \cdot NH_2C_2H_4NH_2$, has a m.p. of 212° ; the other, $COOHC_6H_4COOH \cdot NH_2C_2H_4NH_2 \cdot COOHC_6H_4COOH$, has a m.p. of 232° .
7. With maleic acid, as well as with phthalic acid, ethylenediamine forms - for certain component ratios - resins that have different melting points, depending on the component ratios.

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CONDENSATION OF ACYL ANILIDES WITH CHLORAL

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As was established as long ago as 1874 [1], aromatic hydrocarbons and their hydroxy, alkoxy, and halogen derivatives are easily condensed with chloral by sulfuric acid, forming derivatives of 1,1-diphenyl-2,2,2-trichloroethane. Among the numerous compounds of this class mention must be made of 1,1-n,n'-dichlorodiphenyl-2,2,2-trichloroethane, which has acquired considerable practical importance at the present time as a powerful insecticide.

The application of this condensation to amino compounds remained until recently an inadequately explored field. Wallach [2] and Bdeissneck [3] investigated the reaction of the free bases of primary, secondary, and tertiary aromatic amines with chloral. They found that chloral reacts energetically with the amino group of aniline, forming trichloro-ethylene-N,N-dianiline $\text{CCl}_3\text{CH}(\text{NHC}_6\text{H}_5)_2$, whereas the secondary and tertiary amines enter into an aldol condensation with chloral:



where

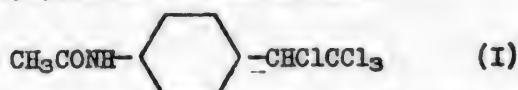
R = Alk; R' = Alk or H.

The reaction of aromatic amines with chloral under the conditions set by Bayer: in the presence of concentrated sulfuric acid, have not been studied up to the present time. It might be supposed that the course of this reaction will differ considerably from that of the reaction with free amines, owing to considerable change in the electron structure of the substituent in salt formation, and hence, a change in its effect upon the mobility of the ring hydrogen. In fact, though aniline itself reacts violently with chloral, its salts do not enter into this reaction: at room temperature aniline sulfate remains unchanged in the presence of sulfuric acid; when the mixture is heated, the chloral is converted to chloralide with the same yield as when the aniline sulfate is not present.

In order to reduce the tendency toward salt formation, we resolved to employ acylated anilines in condensation: a cetanilide, phthalanil, and succin-anil. It was found that acetanilide and phthalanil enter into ring condensation with chloral in the presence of sulfuric acid. Succin-anil does not enter into

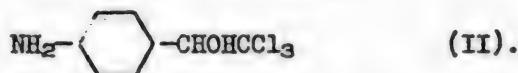
reaction under mild conditions; in severer conditions - heating over a water bath with 98% sulfuric acid - sulfonation takes place.

Acetanilide reacts with 98% sulfuric acid at 95° and heating for several hours, but the reaction is not well defined. To a considerable extent the acetanilide is sulfonated. The acetyl sulfanilic acid present in the solution after the reaction mixture has been treated with water is hydrolyzed, forming sulfanilic acid, when the solution is allowed to stand or more quickly when it is heated. The reaction product, which is insoluble in water, consists largely of 1-p-acetaminophenyl-1,2,2,2-tetrachloroethane:

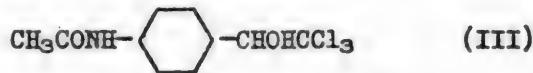


During the reaction a negligible quantity of hydrogen chloride is evolved. It may be assumed that the tetrachloroethane derivative is formed by the reaction of the initial reaction product - the carbinol (III) - with the hydrogen chloride formed in the decomposition of the chloral by sulfuric acid under these conditions. Chattaway and Calvet [4] note the formation of analogous derivatives of tetrachloroethane in the condensation of chloral with anisic acid, and Gätz and Stammbeck [5] made the same observation in synthesizing dichlorodiphenyl-trichloroethane.

Our endeavors to effect a reaction between acetanilide and chloral in the presence of other condensing agents likewise resulted either in the synthesis of p-acetaminophenyltetrachloroethane (by the action of aluminum chloride in hydrogen sulfide), or else the substances did not react at all as we desired, part of the chloral being converted to chloralide, and the acetanilide into N,N-diphenylacetamidin (by the action of POCl_3). Boiling 1-p-acetaminophenyl-1,2,2,2-tetrachloroethane with 20% sulfuric acid hydrolyzes it, forming 1-p-aminophenyl-1-hydroxy-2,2,2-trichloroethane:



This amine can be diazotized, the diazonium salt obtained combining with β -naphthol to form a brick-red dye. Acetylation of the hydroxyamine (II) yields an N-acetyl compound (III):

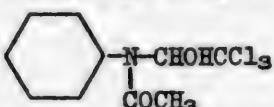


When substances (I), (II), and (III) are heated with a solution of potassium hydroxide, the odor of chloroform is noted: the latter may be detected by the isonitrile reaction after steam distillation. At the same time the reaction liquid acquires powerful reducing properties, rapidly forming a silver mirror with the Tollens reagent. There is no doubt that the substance decomposes under these conditions, as was described by Knöfler and Boessneck [6] for alkyl amino compounds of this type:



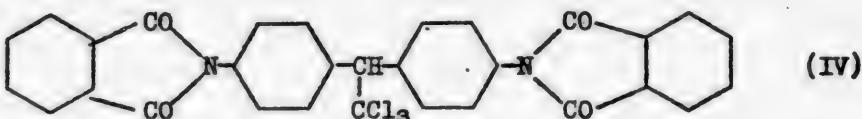
While the present investigation was being carried out, a number of

reports were published by American authors engaged in the synthesis of diamino-diphenyltrichloroethane. Burger, Graf, and Bailey [7] also tried to condense acetanilide with chloral for this purpose. They were able to obtain only 7 g of a substance with a m.p. of 211-213° and the formula $C_{10}H_{10}O_2NCl_3$ from 140 g of acetanilide and 100 g of chloral hydrate; they assigned the conjectural structure of 1-N-acetaminophenyl-1-hydroxy-2,2,2-trichloroethane:

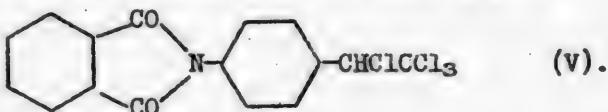


to this substance. Its properties and melting point indicate that this substance corresponds to the carbinol (III) synthesized by us, the formation of which as an intermediate in the synthesis of the tetrachloride (I) is quite probable.

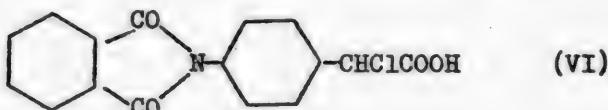
Upon condensation with chloral in the presence of 100% sulfuric acid phthalanil yields a number of substances: 1,1-di-p-phthalanilo-2,2,2-trichloroethane (IV):



is formed when the reaction mass is allowed to stand at room temperature for a long time. The formation of this substance was recently described by Graf and Burger as well [8]. Slight heating with a large excess of sulfuric acid causes the reaction to follow another course. As in the condensation of chloral with acetanilide, hydrogen chloride is liberated and one of the reaction products is 1-p-phthalanilo-1,2,2,2-tetrachloroethane (V), similar to the acetaminotetrachloroethane (I) described above:



Moreover, p-phthalanilchloroacetic acid:



was isolated from the reaction mass.

The formation of substituted chloroacetic acids is likewise observed in similar condensations, such as the condensation of chlorobenzene with chloral [9]. In the acid (VI), the chlorine is easily hydrolyzed, being almost completely split off even in titration by the Volhard method. Action of an excess of dilute alkali causes, together with neutralization of the carboxyl group, the nearly total substitution of hydroxyl for the halogen, as well as the opening of the phthalanil group:



That is why, in titration with an excess of alkali, the acid equivalent is one-third of the molecular weight.

EXPERIMENTAL

1. 1-p-Acetaminophenyl-1,2,2,2-tetrachloroethane (I)

24 g of acetanilide, 12 g of chloral, and 80 ml of 98% sulfuric acid were heated for 5 hours over a water bath at 80°. The reaction mixture darkened; a negligible amount of hydrogen chloride was observed to form.

A thick yellow mass formed when the reaction mass was poured into water; it was isolated from the sulfuric-acid solution, washed several times with water, and dissolved in hot alcohol. In some cases, a small amount of a white crystalline substance — sulfanilic acid — remained undissolved in the alcohol. When the alcoholic filtrate was cooled, crystalline acetaminophenyltetrachloroethane precipitated out. Some more of the latter separated out when water was added to the alcoholic mother liquor. The substance crystallizes from alcohol as brilliant colorless lamellae, m.p. 208°. The yield of pure 1-p-acetaminophenyl-1,2,2,2-tetrachloroethane was 12 g. It is insoluble in water, but easily soluble in hot alcohol, acetone, and acetic acid; it is moderately soluble in ether. The odor of chloroform was noted when it was heated with a dilute solution of potassium hydroxide, yielding a solution that quickly formed a silver mirror when silver nitrate and ammonia were added.

4.009 mg, 3.770 mg substance: 5.901 mg, 5.550 mg CO₂; 1.104 mg, 1.076 mg H₂O.
7.520 mg, 7.265 mg substance: 0.314 ml, 0.299 ml nitrogen (15°, 741 mm)
0.1345 g, 0.1372 g substance: 0.2558 g, 0.2608 g AgCl.

Found %: C 40.14, 40.15; H 3.08, 3.19; N 4.82, 4.77;
Cl 47.04, 47.02.

C₁₀H₉ONCl₄. Calculated %: C 39.88; H 3.01; N 4.66; Cl 47.13.

After the reaction products that were insoluble in water had been removed, the sulfuric-acid filtrate gradually threw down a large quantity of sulfanilic acid upon standing at room temperature. Yield: 8 g.

2. 1-p-Aminophenyl-1-hydroxy-2,2,2-trichloroethane (II)

2 g of acetaminophenyltetrachloroethane (I) was boiled for 8 hours with 30% hydrochloric acid. The substance gradually dissolved; upon cooling the solution, 1.8 g of the aminocarbinolhydrochloride (II) crystallized out in needles.

It was recrystallized from dilute hydrochloric acid.

0.2804 g substance: 9.6 ml 0.1 N AgNO₃ (by the Volhard method)

Found %: Cl' 12.14.

C₈H₈ONCl₃·HCl. Calculated %: Cl' 12.8.

The aqueous solution of the aminocarbinol hydrochloride was dissolved in water and after cooling carefully alkalized with ammonia. The white substance formed, which was insoluble in water, was carefully washed, dried, and recrystallized from benzene; m.p. 111-112°; when fused, it turns into a dark red liquid. 1-p-Aminophenyl-1-hydroxy-2,2,2-trichloroethane is insoluble in water, but soluble in dilute acids, and easily soluble in alcohol, acetone, and ether. It diazotizes, the solution of the diazo compound forming a brick-red dye when combined with β-naphthol.

3.819 mg, 3.198 mg substance: 5.584 mg, 4.701 mg CO₂; 1.200 mg, 1.034 mg H₂O.
7.960 mg, 8.705 mg substance: 0.412 ml, 0.441 ml N₂ (20°, 737 mm).

Found %: C 39.88, 40.09; H 3.52, 3.62; N 5.82, 5.70.

C₈H₈ONCl₃. Calculated %: C 39.98; H 3.52; N 5.82.

3. 1-p-Acetaminophenyl-1-hydroxy-2,2,2-trichloroethane (III)

To a solution of 2.4 g of the aminocarbinol (II) in 10 ml of ether there was added, with chilling, 2.04 g of acetic anhydride, and two hours later the crystalline acetyl compound that settled out was filtered off. Yield: 2 g. Another 0.5 g of the substance was isolated by evaporating the mother liquor. It was doubly crystallized from acetic acid; m.p. 217°.

0.1837 g, 0.1670 g substance: 0.2777 g, 0.2522 g AgCl.

Found %: Cl 37.40, 37.36.

C₁₀H₁₀O₂NCl₃. Calculated %: Cl 37.56.

4. 1,1-Di-p-phthalanilo-2,2,2-trichloroethane (IV)

14 g of phthalanil (recrystallized from alcohol, m.p. 213°), 7 g of chloral, and 75 g of 100% sulfuric acid were mixed together at room temperature until all the phthalanil had dissolved and then heated for 21 hours at 30°. The reaction mixture was then poured over 250 g of ice; the substance that separated out was filtered off, washed with water, air-dried, and recrystallized from alcohol. Yield: 8 g of di-p-phthalanilo-2,2,2-trichloroethane. For final purification it was recrystallized from ether and then again from alcohol. Colorless crystals, m.p. 98-99°. Burger and Graf cite a m.p. of 97-99° for this preparation, which they synthesized under similar conditions.

5. 1-p-Phthalanilo-1,2,2,2-tetrachloroethane (V)

6.5 g of chloral, 20 g of phthalanil, and 300 ml of 100% sulfuric acid were heated for 21 hours to 35-40° over a water bath, and then poured over ice. The deposit that settled out was dissolved in ether, the ether solution then being washed with water, bicarbonate solution, and again with water, and dried with sodium sulfate. After some of the ether had been driven off from the solution, a crystalline substance settled out; this was separated from the dark ethereal mother liquor and washed with cold ether. Yield: 1.5 g of a nearly white substance with a m.p. of 162-165°. Recrystallization from ether yielded pure 1-p-phthalanilo-1,2,2,2-tetrachloroethane with a m.p. of 175-176°. A silver mirror is formed when this is heated with dilute potassium hydroxide, and a solution of silver nitrate with ammonia is added to it. When the substance is reacted with a 25% solution of potassium hydroxide, a violent reaction takes place, accompanied by considerable tarring; the odor of chloroform

is noticed at the beginning of this reaction.

3.215 mg substance: 5.812 mg CO₂; 0.752 mg H₂O.
10.719 mg, 11.912 mg substance: 2.79 ml, 3.12 ml 0.01 N H₂SO₄ (Kjeldahl)
Found %: C 49.30; H 2.62; N 3.64, 3.67.
C1eH9O2NCl4. Calculated %: C 49.36; H 2.33; N 3.60.

6. p-Phthalanilchloroacetic Acid (VI)

To the solution washed with bicarbonate in the previous experiment there was added dilute sulfuric acid until Congo indicator gave an acid reaction. Crystalline p-phthalanilchloroacetic acid was precipitated out. The yield of the air dried substance was 2.5-4 g, m.p. 193°. It is soluble with difficulty in hot alcohol, acetone, benzene, and chloroform. It settles out of these solvents upon cooling in the form of precipitates that are hard to filter. It is recrystallized by solution in a large quantity of ether and precipitation with pentane or from 80% acetic acid. It is obtained as colorless tiny needles, with a m.p. of 218.5-2.8°, after fivefold recrystallization.

When a weighed batch of the acid was treated with an excess of 0.1 N potassium hydroxide and then neutralized with 0.1 N hydrochloric acid, we found:

0.1030 g substance: 8.7 ml 0.1 N KOH.
0.3398 g substance: 30.08 ml 0.1 N KOH.
Found :
C1eH10O4NCl. Calculated M_r/3: 105.2.
3.034 mg, 3.449 mg substance: 6.780 mg, 7.736 mg CO₂; 0.923 mg, 0.976 mg H₂O.
9.139 mg, 9.112 mg substance: 2.89 ml, 2.88 ml 0.01 N H₂SO₄ (Kjeldahl).
0.1102 g substance: 0.0491 g AgCl (Carius).
Found %: C 60.94, 61.17; H 3.14, 3.17; N 4.43, 4.42;
Cl 11.02.
C1eH10O4NCl. Calculated %: C 60.86; H 3.17; N 4.44; Cl 11.25.

Determination of Hydrolyzable Chlorine

0.1030 g substance: 2.8 ml 0.1 N AgNO₃ (Volhard method)
Found %: Cl 9.66.

SUMMARY

1. In studying the reaction of the acyl anilides with chloral in the presence of sulfuric acid it was found that acetanilide and phthalanil enter into a condensation reaction with chloral, whereas succinanil does not react with chloral under the conditions of the experiments performed.

2. The reaction of acetanilide with chloral yielded 1-p-acetaminophenyl-1,2,2,2-tetrachloroethane; from the latter 1-p-aminophenyl-1-hydroxy-2,2,2-trichloroethane was synthesized, and from the latter 1-p-acetaminophenyl-1-hydroxy-2,2,2-trichloroethane.

3. Di-1-phthalanilo-2,2,2-trichloroethane, 1-phthalanilo-1,2,2,2-tetrachloroethane, and phthalanilchloroacetic acid were synthesized by the reaction

of phthalanil with chloral.

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RESEARCH IN COMPOUNDS OF HIGH MOLECULAR WEIGHT

XXII. THE POLYCONDENSATION OF BENZYL CHLORIDE

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The polycondensation reaction of benzyl chloride when acted upon by aluminum chloride was first described by Perkin and Hodkinson [1]. It was subsequently investigated by Friedel and Crafts [2], Schramm [3], Ushakov and Kon [4], and Jacobson [5]. The action of ferric chloride, aluminum chloride and zinc chloride was studied by Ushakov and Kon [4]. They found that ferric chloride is superior to aluminum chloride in that it yields soluble polycondensation products.

Polycondensation of Benzyl Chloride

The catalysts tried out by us included: aluminum chloride, ferric chloride, and zinc chloride. The reaction was effected in a round-bottomed flask fitted with a reflux condenser; outwardly, the reaction was identical for all these three catalysts, the sole difference being that with zinc chloride, preheating to 80-90° was required to start the reaction, whereas the reaction set in at room temperature when aluminum or ferric chloride was used. The reaction was accompanied by considerable frothing, and it was brought to a conclusion while heated over a water bath. After cooling, the flask was found to contain a friable solid mass, which was freed from residues of benzyl chloride by steam distillation and from the catalysts by washing with hydrochloric acid and then with water.

This yielded a solid, friable resin, which was identified by its solubility, melting point, and molecular weight (by the cryoscopic method). As is shown by Table 1, the properties of the product are largely governed by the catalyst employed.

Aluminum chloride yields an orange powder that is only partially soluble in benzene. This product is highly refractory, beginning to soften only at 220-230°. The molecular weight of the soluble part of the resin turned out to be close to 2000, agreeing with Jacobson's data [5].

When zinc chloride was employed, we got a solid, light-yellow powder. It dissolves completely in benzene and fuses as low as 63-95°.

When benzyl chloride is polycondensed in the presence of ferric chloride, we get a greenish-yellow powder, almost fully (85-90%) soluble in benzene and in-

Table 1
Products of the Polycondensation of Benzyl Chloride

Test No.	Catalyst	Weight of benzyl chloride, g	Weight of catalyst, g	Molar ratio C ₆ H ₅ CH ₂ Cl to catalyst	Resin Yield		Molecular Wt.	Temperature	
					in g	% of theory		Softening sets in	Appearance of meniscus
1	AlCl ₃	12.7	0.266	50:1	8.0	88.5	2010	220°	does not fuse
2		12.7	1.33	10:1	8.1	90.0	1945	230	
3	FeCl ₃	63.5	0.202	400:1	42.1	93.3	2600	72	108°
4		12.7	1.62	10:1	8.4	92.8	2500	71	106
5	ZnCl ₂	12.7	0.137	100:1	8.1	89.5	2100	65	95
6		12.7	0.273	50:1	7.9	87.5	2100	63	92

insoluble in alcohol or ether. Its molecular weight is higher than that of the products synthesized with aluminum or zinc chloride.

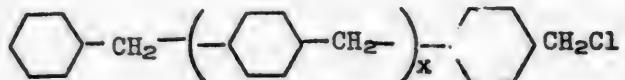
As is seen from Table 1, variation in the quantity of catalyst used has no effect upon the properties and yield of the products. Increasing the amount of the catalyst merely causes the color of the product to grow gradually darker. The optimum benzyl chloride: catalyst ratio must be taken to be 200:1.. In this case the reaction is energetic enough, the yield of product being close to the theoretical value after 3 hours have gone by.

Structure of the Polycondensation Products

Friedel and Crafts [10], as well as Radziewanowski [8], held that the product of benzyl chloride polycondensation is the polymer of benzylene (C₆H₅=CH₂)_x; Ushakov and Kon [4] assigned it the formula (C₆H₅CH=CHC₆H₅)_x. Evidently, the polycondensation of benzyl chloride is quite similar to the usual Friedel-Crafts syntheses, being directly due to the presence within the molecule of a mobile chlorine atom, as well as of an aromatic ring that can be transformed by the action of another molecule of benzyl chloride. This opinion has already been voiced by Jacobson [5] who conjectured that the macromolecule of the polymer was built up of the following structural units:



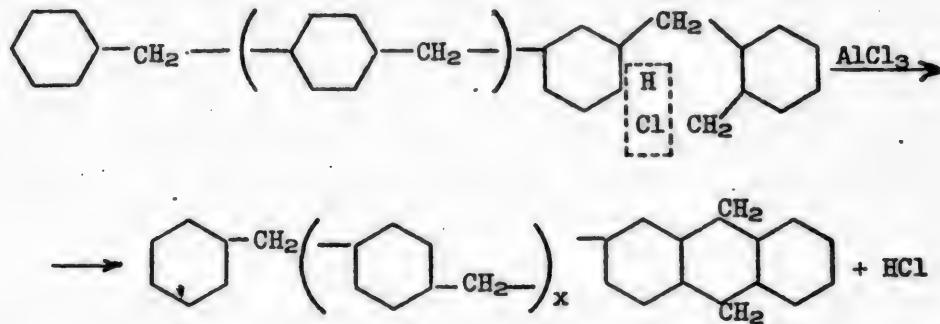
The first stages of the polycondensation of benzyl chloride were tracked down by Wertyporoch and Farnik [11], who succeeded in isolating p- and o-chloromethyldiphenylmethanes by allowing aluminum chloride to act upon benzyl chloride in nitrobenzene at a temperature of -15°. Hence, we may assume that the resin macromolecule is constructed as follows:



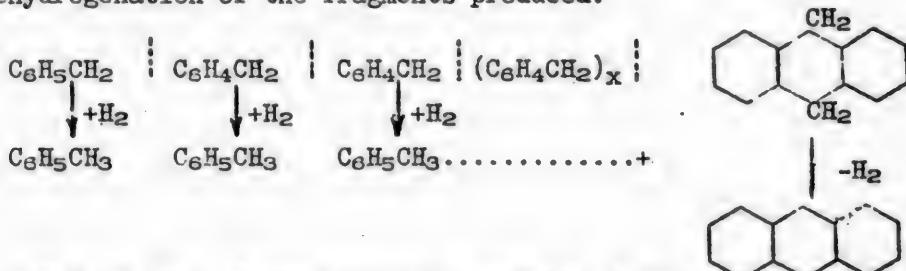
It probably may be branched, owing to the possibility of secondary alkylation of a single benzene ring.

To confirm this view, we effected the destructive distillation of the product synthesized with ferric chloride. This yielded 8.0 g of distillate and 20.0 g of a charred residue from 30 g of the product. The remaining 2 g were accounted for by gases and losses. Distillation of the distillate yielded 4.1 g of pure toluene, b.p. 109-111°, d_4^{25} 0.8685; n_D^{20} 1.475, and 1.8 g of a fraction that distilled over at 300-360° as a yellow paste. It was repeatedly recrystallized from acetic acid, yielding 0.5 g of pure anthracene with a m.p. of 213°, identified by its picrate, which fused at 137°, and by its oxidation product, with a m.p. of 278-280°, which corresponds to anthraquinone. Distillation of the 300-360° fraction left 2.0 g of a reddish brown, semisolid, with a molecular weight of 320, in the flask.

The formation of anthracene indicates that as the chain gradually lengthens, ortho substitution effects an internal closing of the ring:



Pyrogenetic cleavage of this chain ought to yield both toluene and anthracene as a result of rupturing the bonds, with simultaneous hydrogenation and dehydrogenation of the fragments produced:



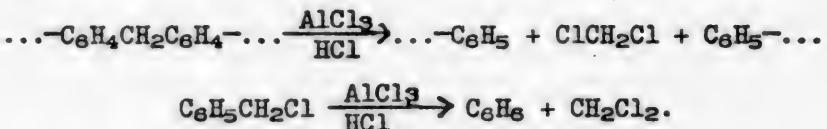
If this sort of ring closure, with the formation of a dihydroanthracene ring occurred in each chain, the anthracene yield as a result of pyrolysis would be 6.85%, in view of the resin's molecular weight of 2600. We actually obtained 1.7%. On the other hand, Ushakov and Kon [4] found the chlorine content of the resin to be 0.4-0.6%, whereas it theoretically should be 1.36%. These figures confirm our conclusion that internal closure of the dihydroanthracene ring occurs in the portion of the resin macromolecule that is terminated by ortho-substituted groups. It is apparent that the other portion of the molecule, which is terminated by para-substituted rings, escapes cyclization and terminates in a chlorine atom.

Destruction of the Polycondensation Products

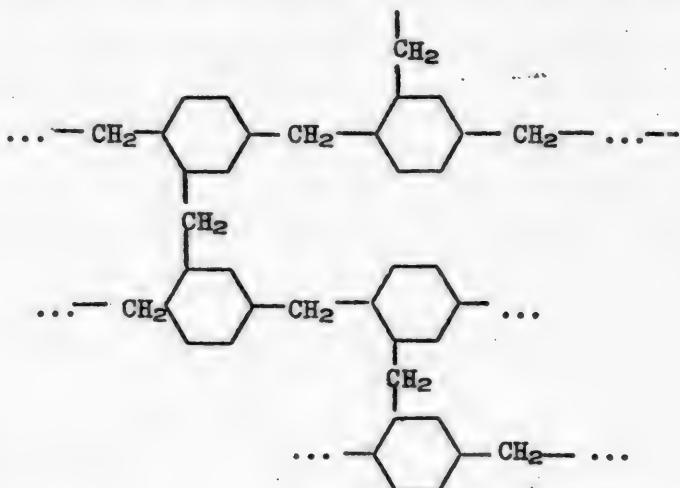
We also carried out the destruction of the polycondensation products by heating them with benzene in the presence of aluminum and ferric chlorides.

When 9.0 g of the product (with a molecular weight of 2620) was heated with ten times its weight of benzene and aluminum chloride, we got 3.5 g of pure diphenylmethane, b.p. 255-260°, m.p. 24.0°, d_4^{20} 1.002, n_D^{20} 1.5790, and 4.5 g of a product with a molecular weight of 1320. Thus, aluminum chloride effects extremely thorough destruction. Ferric chloride proved to be much weaker in its action. Neither heating the product with benzene and ferric chloride for a long time, nor simultaneously passing hydrogen chloride through the mixture resulted in the formation of products of low molecular weight; all that happened was the lowering of the molecular weight (from 2600 to 2000-2200). Thus, ferric chloride effects much less destruction than aluminum chloride.

This fact is, we believe, also the reason for the sharp difference in the properties of the products synthesized with these catalysts. During the process of chain growth, aluminum chloride actually exerts a stronger destructive effect upon both the chains and the benzyl chloride. As a result, it becomes possible for methylene chloride to be formed:



The latter compound already has two atoms of chlorine in its molecule and can react with the benzene rings of two linear macromolecules, linking them together in a three-dimensional structure that is insoluble and infusible:



This is wholly impossible in the case of ferric chloride, which yields a soluble resin, since it is unable to catalyze the alkylation reaction within the benzyl chloride ring at the ortho position.

Polycondensation of Benzyl Chloride With Various Admixtures of Benzene
in the Presence of Ferric Chloride

The reaction of benzyl chloride with benzene in the presence of aluminum chloride has been investigated by Friedel and Balsohn [6], Friedel and Crafts [7], and Radziewanowski [8]. In addition to the products of high molecular weight, these authors obtained diphenylmethane, and ortho and para dibenzylbenzene. In the presence of ferric chloride, Wertyporoch, Kowalski, and Roeske [9] obtained diphenylmethane, triphenylmethane, two oily products, and a resin of high molecular weight.

Hence, when benzyl chloride, benzene, and ferric chloride are mixed together, two competing processes take place: the polycondensation of benzyl chloride and the latter's reaction with benzene.

In all our experiments we kept the ferric chloride: benzyl chloride ratio constant at 1:100, while varying the amount of benzene added within wide limits: from 2 mol.% to 1000 mol.% of benzyl chloride. The first four of the experiments listed in Table 2 were carried out like the preceding ones. In the last three experiments, the method used to separate the reaction products was changed; they were extracted with benzene and then subjected to distillation. After the benzene had been driven off, we collected a 240-270° fraction and then a 280-360° fraction. The first fraction was redistilled in vacuum, yielding crystalline diphenylmethane with a m.p. of 25°, d_{14}^{20} 1.004, n_D^{20} 1.5791; a repeated distillation of the second fraction yielded an oily distillate, which soon hardened into a grainy-crystalline paste. Treating this paste with ether and recrystallizing it several times from alcohol yielded beautiful, shiny, acicular crystals with a m.p. of 79-84°, which corresponds to a mixture of ortho and para dibenzylbenzenes [12]. We did not separate the latter.

Besides these two fractions, in some of the experiments vacuum distillation yielded a small quantity of thick oily liquids with a molecular weight of 315-340, which boiled at 250-300° at 10 mm of mercury column. They are probably identical with the oils obtained by Wertyporoch, Kowalski, and Roeske [9], and we did no further research on them. The distillation residue was a tar. It was found that the yields of the reaction products and their properties were largely governed by the amount of excess benzene. The results of these experiments are given in Table 2, the amount of benzyl chloride being kept constant at 12.7 g for all the experiments, and that of ferric chloride at 0.162 g.

The curves of Fig. 1 have been plotted from the data of Table 2.

As the quantity of benzene added is increased, the yield of tar declines uninterruptedly, whereas the diphenylmethane yield rises, reaching 42% for a ten-fold excess of benzene. The curve of dibenzylbenzene yield passes through a maximum.

The predominance of the tar, even when the benzene: benzyl chloride ratio is 1:1, indicates that benzyl chloride has a greater tendency toward substitution ring reactions than benzene; this is evidently due to the fact that the chloromethyl group exerts an activating effect on the benzene ring.

Up to an excess of 20 mol.% of benzene in terms of benzyl chloride the polycondensation products are solids, with gradually lower melting points. But at 40 mol.% of benzene we get a viscous mass, whose consistency grows increasingly

Table 2

Yields and Properties of the Products of the Condensation of Benzyl Chloride with Benzene in the Presence of FeCl_3

Test No.	Benzene in mol. % of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	Yield of product		Molecular weight of product	M.p. of product Softening sets in Meniscus forms	Yield of diphenylmethane Grams	Yield of dibenzylbenzenes Grams	% of theory	Yield of oil with $M=315-340$
		Grams	% of theory						
1	2.0	8.5	94.0	2000	60 90	-	-	-	-
2	5.0	8.2	90.7	1700	55 85	-	-	-	-
3	10.0	7.8	86.4	1305	40 70	-	-	-	-
4	20.0	7.6	84.0	920	33 65	-	-	-	-
5	50.0	6.3	70.0	510	liquid	2.5	12.5	3.2 25.0	-
6	100.0	5.65	60.0	430	"	3.86	23.0	2.0 15.5	0.7g
7	1000.0	2.7	30.0	420	"	7.0	42.0	1.45 11.3	1.7g

fluid as the amount of benzene continues to increase. The products of the first few experiments are soluble only in benzene, chloroform, and carbon disulfide, whereas the latter ones are also soluble in alcohol and ether.

Evaluation of Results

Some time ago one of the present authors, together with Rafikov [13] and Golubev [14] showed that in the polycondensation of hexamethylenediamine with adipic acid the molecular weight of the polyamide synthesized largely depends upon the excess of adipic acid, the initial small batches of the excess component exerting an extremely pronounced effect. This was also demonstrated by one of the present authors, together with Kolesnikov and Kharchevnikov, in the polycondensation reaction of benzene with dichloroethane [15].

In the reaction investigated by us, the benzene may quite justifiably be looked upon as the excess component, since the benzyl chloride molecule has both the active chlorine atom and the benzene ring. Our results, which indicate the change in molecular weight as a function of the amount of added benzene, are pictured in Fig. 2.

They exhibit striking agreement with the data of the authors mentioned above. Indeed, even a small amount of benzene, even as little as 2 mol.%, lowers the product's molecular weight from 2650 to 2000, i.e. by 25%. This effect tends to diminish, becoming practically zero at 40-50 mol.% of benzene.

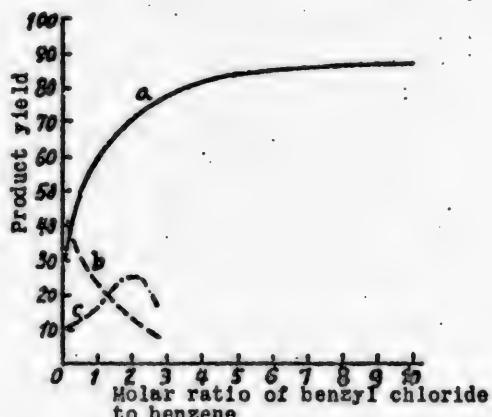
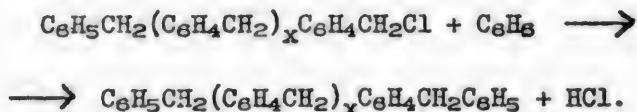


Fig. 1. Product yielded as a function of the quantity of benzene added.

a-Yield of tar; b-Yield of diphenylmethane
c-Yield of dibenzylbenzene.

Thus, even for such polycondensation products as are obtained by the action of ferric chloride upon benzyl chloride, which are quite different in character from the polyamide resins, we see a quite similar picture, which tends to prove the universality of the laws governing many polycondensation processes, despite their apparent differences.

Evidently, the mechanism of the action of the excess component in this case will be the same as was assumed for the polyamide resins [14]. In fact, benzene can also cause the destruction of the resin in the presence of ferric chloride, as we saw above. Evidently, the benzene molecules not only interrupt the growth of the chains by reacting with the chlorine terminal atom:



but also rupture the chain, decreasing its length.

Thereafter, the subsequent growth of the chain becomes possible only by means of the successive alkylation of the substituted benzene ring by the molecules of benzyl chloride, and this is why the rate of growth of such chains drops rapidly.

SUMMARY

1. The polycondensation reaction of benzyl chloride was investigated.
2. It was found that a dihydroanthracene ring is the last link in the macromolecule chain, and the mechanism of the formation and the structure of the products of the polycondensation of benzyl chloride were explained.
3. The polycondensation reaction of benzyl chloride in the presence of benzene was investigated.
4. It was found that the molecular weight of the products formed drops as the quantity of benzene is increased, the first small benzene batches exerting a very pronounced effect.

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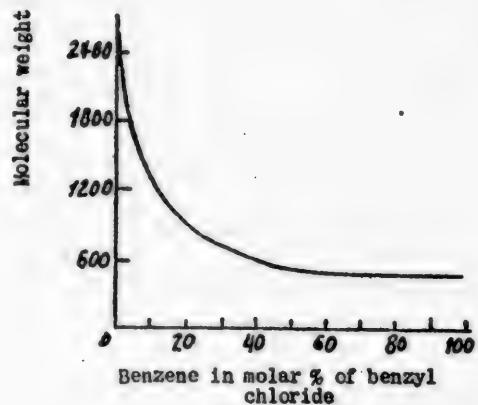


Fig. 2. Molecular weight as a function of the quantity of benzene added.

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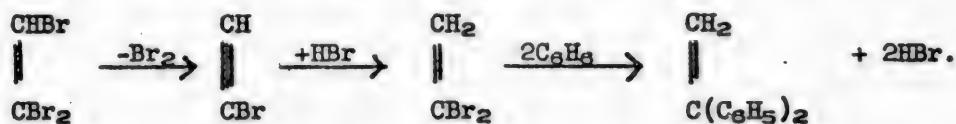
THE MECHANISM OF THE FRIEDEL-CRAFTS REACTION

IX. THE REACTION OF TRICHLOROETHYLENE WITH BENZENE

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By reacting tribromomethylene with benzene in the presence of aluminum bromide, Anschütz [1] synthesized 1,1-diphenylethylene and triphenylmethane. The formation of these products was quite unexpected, and to explain the formation of 1,1-di-phenylethylene Anschütz proposed the following, quite artificial, equation for the reaction in which diphenylethylene is formed:



He did not explain why bromine was split off from the tribromoethylene, nor did he provide any experimental proof of this equation. Anschütz was compelled to admit that the formation of triphenylmethane was completely incomprehensible.

We endeavored to analyze the mechanism of this reaction. To this end we reacted trichloroethylene with benzene at the boiling point of the reaction mixture. The proportions of the initial substances were as follows: 20 moles of benzene and 1 mole of aluminum chloride per mole of trichloroethylene. These are about the proportions employed by Anschütz.

Decreasing the ratio of aluminum chloride to 1/2-1/5 mole per mole of trichloroethylene reduced the product yield.

The reaction yielded a solid, dark-brown product that fused at about 45-55°. It is easily crushed to a powder, which conglomerates upon standing. It is easily soluble in benzene, chloroform, carbon tetrachloride, and acetone, but poorly soluble in methanol and ethyl alcohol. When heated it dissolves in isobutyl alcohol and petroleum ether.

We were unable to isolate individual crystalline substances from the reaction product by recrystallization from various solvents. Every time the whole brown product separated out of the solution at once. The carbon and hydrogen content of the substance, as well as its molecular weight, correspond to the formula $\text{C}_{40}\text{H}_{32}$.

Dry distillation of the product yielded two fractions: one liquid and the other

solid. It was noticed that the yield of liquid and solid fractions depends upon the duration of the reaction between the benzene and the trichloroethylene. When the reaction time is lengthened, the yield of the liquid fraction is diminished while that of the solid fraction rises.

After distillation, we isolated the following constituents of the liquid fraction: a liquid that boils at 262-264°, whose constants are in good agreement with those given in the literature for diphenylmethane, and a solid crystalline substance that fuses at 92° (from acetic acid) and at 78° (from benzene), which corresponds to triphenylmethane crystallized with one molecule of benzene [2]. The triphenylmethane was subsequently identified by its oxidation to triphenylcarbinol. The solid product of the second fraction produced by dry distillation proved to be anthracene, fusing at 212-214°. Its picrate fuses at 137-139°; oxidizing it yields anthraquinone.

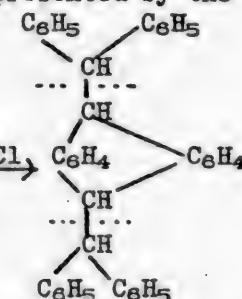
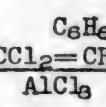
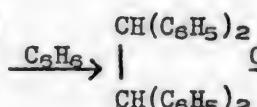
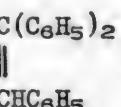
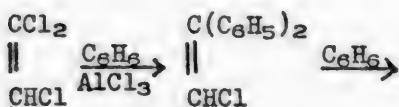
In view of the fact that the physical properties of diphenylmethane and 1,1-diphenylethylene are fairly close, we subjected the liquid fraction to more detailed investigation.

Besides determining the boiling point, specific gravity, and refractive index, we effected a series of chemical transformations to decide which of these two substances we had produced.

An excellent method for identifying 1,1-diphenylethylene is the production of its crystalline dimer by the action of dimethyl sulfate as described by V.N.Belov [3]. That is the method we used. All of our efforts met with failure however, and we were unable to synthesize the crystalline dimer of 1,1-diphenylethylene from our fraction.

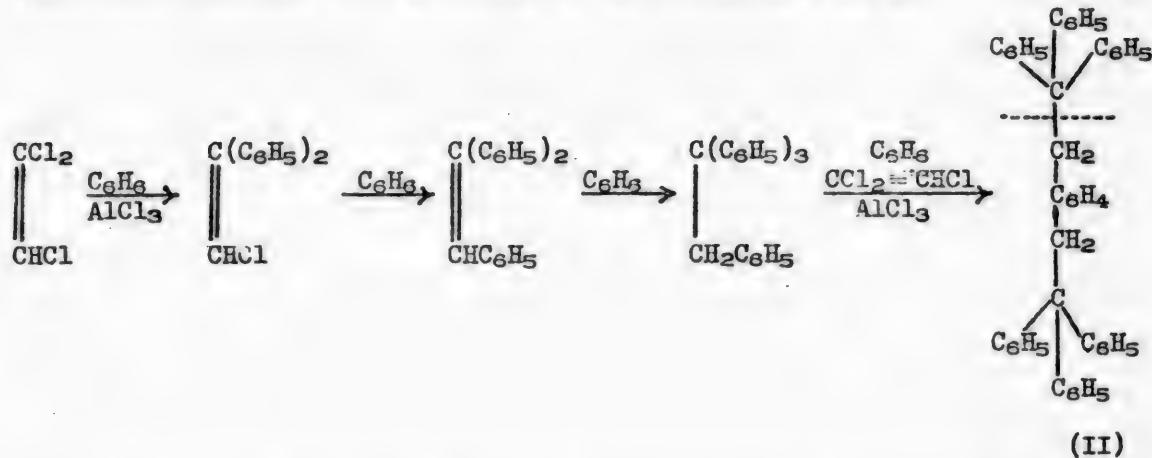
We effected a comparative bromination of our fraction and of a sample of 1,1-diphenylethylene synthesized independently. Bromination of the 1,1-diphenylethylene required about 40 times as much bromine as did that of our fraction. And, finally, the formation of anthracene when our fraction was heated with aluminum chloride [4] demonstrated clearly enough that we had not synthesized 1,1-diphenylethylene, but diphenylmethane; as we know, the latter reaction is characteristic of diphenylmethane [4].

These results justify the definite assertion that Anschütz' data are in error, since the reaction of trichloroethylene with benzene evidently yields a product that is a mixture of polycyclic compounds. Only upon the thermal decomposition of this initial substance are diphenylmethane, triphenylmethane, and anthracene obtained. The formation of this product may be represented by the following diagram, as we see it:



(I)

Besides the possible formation of the bis-9,10-(diphenylmethyl)-9,10-dihydroanthracene (I) illustrated here, it is probable that the reaction may also follow another course, resulting in the formation of bis-1,4-(1,1,1-triphenylethyl)-benzene (II) according to the following diagram:



The points of rupture during dry distillation are denoted by dotted lines.

The first diagram elucidates the formation of a product whose dry distillation yields diphenylmethane and anthracene; the second diagram showing a product that yields triphenylmethane.

In these proposed diagrams, the intermediate reaction product in the first stage is a compound such as 1,1-diphenyl-2-chloroethylene. To settle this problem we synthesized 1,1-diphenyl-2-chloroethylene separately by chlorinating 1,1-diphenylethylene.

Reaction of the latter with benzene in the presence of aluminum chloride yielded a tarry product that outwardly resembled the product of the reaction between trichloroethylene and benzene. This product was subjected to dry distillation, yielding diphenylmethane, triphenylmethane, and anthracene. This led us to conclude that 1,1-diphenyl-2-chloroethylene is the first intermediate product in the reaction of trichloroethylene with benzene.

EXPERIMENTAL

1. Reaction of Trichloroethylene With Benzene

Into a three-necked flask, fitted with a stirrer provided with a mercury seal, a reflux condenser, and a dropping funnel, there are placed 30 g of aluminum chloride and 300 ml of benzene. The mixture is brought to a boil, after which 30 g of trichloroethylene, dissolved in 100 ml of benzene, is gradually added. The flask is heated over a boiling water bath for a further 1.5 hours after the benzene solution of trichloroethylene has been added. The overall duration of the reaction is 3-4 hours. The reaction mixture is then poured off into dilute hydrochloric acid; the top layer is removed and steam-distilled for 10 hours. After the steam distillation is over, a tarry, dark-brown product remains in the flask. B.p. 45-55°. Yield: 40-50 g. The substance contains no chlorine.

5.180 mg, 4.710 mg substance: 17.714 mg, 16.056 mg CO₂; 2.910, 2.670 mg H₂O.
Found %: C 93.32, 93.03; H 6.28, 6.34.
C₄₀H₃₂. Calculated %: C 93.75; H 6.25.

Determination of the reaction product's molecular weight (cryoscopically in benzene):

0.2900 g substance: 12.5508 g benzene: Δt 0.32°.
0.2406 g substance: 12.5508 g benzene: Δt 0.232°.
Found: M 400, 425.
C₄₀H₃₂. Calculated: M 512.

Isobutyl alcohol, petroleum ether, mixtures of ethyl and isobutyl alcohol, ethyl alcohol, and sulfuric ether were tested for recrystallizing the reaction product. No crystalline deposit was obtained in any of these. Precipitation with ethyl alcohol yielded the same quantity, more or less, of the tar, depending on the ratio between the alcohol and the second solvent.

2. Dry Distillation of the Reaction Product

30 g of the dried tar was subjected to dry distillation in a retort heated over an open flame. The following fractions were collected.

- I. 170-320°, 12.5 g - a dark brown liquid.
- II. 320-370°, 6 g - a solid red mass.

10 g of coke remained in the retort.

We noticed that the duration of the reaction affected the quantitative composition of the products of the pyrolysis of the tar. Though the tarry product itself changes somewhat (melting point and molecular weight rise slightly) when the reaction time is prolonged, the relative amounts of the products of pyrolysis change fairly strikingly. When the length of the reaction is increased from 2 to 6 hours, the quantity of the liquid fraction obtained in dry distillation is cut to one-third, the solid fraction increasing about three-fold.

Investigation of Fraction I. Distillation in vacuum (7 mm) yielded the following fractions:

B.p. 120-140° - a light yellow liquid.
B.p. 150-200° - a white crystalline substance.

a) Investigation of the 120-140° fraction. Redistillation yielded a colorless liquid that boiled at 262-264°.

d₄¹⁵ 1.0104; n_D¹⁵ 1.5780; MR_D 55.00. MR_D computed for diphenylmethane: 55.03.

Since Anschütz asserted that the reaction of triboromethylene with benzene yielded 1,1-diphenylethylene, which we considered to be doubtful, we subjected this fraction to especially careful investigation. As has been stated above, 1,1-diphenylethylene when acted upon by dimethyl sulfate, yields a crystalline dimer [3] that fuses at 138°. We therefore heated 1.2 g of the fraction

with 0.9 g of dimethyl sulfate for five hours over a boiling water bath. No dimer of 1,1-diphenylethylene was obtained. The reaction was repeated several times.

It is known that 1,1-diphenylethylene adds bromine easily, whereas diphenylmethane does so with great difficulty.

0.5 g of 1,1-diphenylethylene prepared separately was dissolved in 5 ml of carbon tetrachloride. A 0.5% solution of bromine in carbon tetrachloride was added to the solution obtained until the instantaneous decolorization ceased. Bromine consumption: 12 ml. For the sake of comparison, 0.5 g of our fraction was likewise dissolved in carbon tetrachloride and titrated with the bromine solution until the solution was noticeably colored. Bromine consumption: 0.5 ml. We thus convinced ourselves that our fraction is not 1,1-diphenylethylene.

Anthracene from diphenylmethane. 5 g of diphenylmethane and 6 g of aluminum chloride were heated together for 5 hours over a boiling water bath. The reaction mixture was then broken down with weak hydrochloric acid, and the oil extracted with benzene. The benzene layer was removed and dried with calcium chloride, the benzene driven off, and the residue distilled in vacuum. A fraction boiling in the 190-200° interval at 10 mm was collected. The yield of crude anthracene was 1 g, or 50% of the theoretical.

Recrystallization from acetic acid yielded 0.4 g of anthracene, fusing at 212-213°, which is close to the literature data for anthracene [5]. With picric acid it forms a picrate that fuses at 138-140°, with is in agreement with the figure cited in the literature [6].

b) Investigation of the 150-200° fraction. Recrystallization from acetic acid yielded crystals that fused at 92°; recrystallization from benzene yielded crystals that fused at 78°, which is the melting point of triphenylmethane crystallized with one molecule of benzene, [2]

Oxidation of triphenylmethane to triphenylcarbinol. 2.5 g of triphenylmethane (from the 150-200° fraction), 15 ml of water, 11.2 g of potassium bichromate, and 10 ml of concentrated H₂SO₄ were boiled together for 12 hours. When the contents of the flask were diluted with water, a white deposit settled which was filtered out and recrystallized from acetic acid. The white acicular crystals fused at 162°, which corresponds to the figure given in the literature for triphenylcarbinol [7].

Investigation of Fraction II. Fraction II was distilled in vacuum and then recrystallized from acetic acid. We obtained crystals with a m.p. of 212-214°, which is close to the melting point of anthracene.

Synthesis of anthracene picrate. 0.2 g of Fraction II and 0.25 g of picric acid were carefully mixed together in a small watch glass and cautiously melted. This yielded a red substance that melted at 137-139°, which is the melting point of anthracene picrate.

Synthesis of anthraquinone. 0.5 g of Fraction II was dissolved in the smallest possible quantity of acetic acid, 3 ml of concentrated H₂SO₄ was added, and the solution was saturated in the cold with potassium chromate. Then the contents of the flask was boiled for 5-10 minutes and diluted with water. The precipitate was filtered out and recrystallized from acetic acid. This yielded

the crystals of anthraquinone, fusing at 281°.

3. Synthesis of 1,1-Diphenylethylene [8]

66 g of aluminum chloride and 200 ml of benzene were placed in a three-necked flask fitted with a stirrer, provided with a mercury seal, a reflux condenser, and a dropping funnel. 48.4 g of vinylidene chloride, dissolved in 100 ml of benzene, were added from the dropping funnel with constant stirring. The reaction causes heat to be evolved and hydrogen chloride to be liberated. During the reaction the flask was cooled by water; the adding of the vinylidene chloride took 2 hours. After this had been completed, the reaction mixture was stirred for another 0.5 to 1 hour at room temperature and then decomposed by dilute hydrochloric acid. The top layer was removed and dried with calcium chloride, and its benzene driven off. The residue was distilled in vacuum. A fraction boiling in the 125-130° range at 10 mm is collected. Yield: 15 g of 1,1-diphenylethylene.

4. Synthesis of 1,1-Diphenyl-2-chloroethylene

30 g of 1,1-diphenylethylene was placed in a test tube with an outlet fitted with a bubbler, through which chlorine was passed until no more hydrogen chloride was evolved. The reaction product was distilled in vacuum, a fraction boiling in the 170-175° range at 7 mm being collected.

The yield of 1,1-diphenyl-2-chloroethylene was 25 g (69.9% of theory).

5. Reaction of 1,1-Diphenyl-2-chloroethylene with Benzene

15.5 g of aluminum chloride and 200 ml of benzene were placed in a three-necked flask provided with a stirrer fitted with a mercury seal, a reflux condenser, and a dropping funnel. The contents of the flask were heated to boiling, after which a solution of 25 g of 1,1-diphenyl-2-chloroethylene in 100 ml of benzene was gradually added. As soon as the very first drops of 1,1-diphenyl-2-chloroethylene were added, the reaction mixture turned red, gradually growing darker and darker. Hydrogen chloride was liberated violently. The reaction was continued for 4 hours over a boiling water bath. After the reaction mixture had been decomposed by dilute hydrochloric acid, the top layer was removed and steam-distilled for 10 hours.

What was left in the flask was a brown tar, which was subjected to dry distillation, two fractions being recovered:

- I. From 170 to 340°,
- II. From 340 to 400°.

What was left in the retort was coke.

These fractions were in turn distilled in vacuum. The following fractions were recovered from Fraction I.:

- 1) B.p. 120-123° at 10 mm;
- 2) B.p. 160-190° at 10 mm.

The first fraction was found to have a b.p. of 260-263°.

This fraction was then boiled with aluminum chloride, yielding anthracene, which fused at 213° (after recrystallization from acetic acid). This proved that the first fraction was diphenylmethane.

The second fraction was first recrystallized from acetic acid, and then from benzene. The former procedure yielded crystals that melted at 92° , whereas the latter yielded crystals that melted at 78° , which agrees with the figures cited for triphenylmethane.

Fraction II was likewise vacuum-distilled. This yielded a yellow substance, which upon recrystallization from acetic acid in turn yielded yellow platelets that fused at 212° . When this substance was reacted with picric acid by the method described above, we got a picrate that fused at 137 - 139° .

Fraction II was thus identified as anthracene.

SUMMARY

1. The reaction of trichloroethylene with benzene in the presence of aluminum chloride was investigated.
2. It was found that the reaction of trichloroethylene with benzene gives rise to polycyclic condensation products.
3. It was established that diphenylmethane, triphenylmethane, and anthracene are formed as the result of the thermal decomposition of the condensation products of trichloroethylene and benzene.
4. The probable diagram of the condensation reaction of trichloroethylene and benzene is set forth.
5. It was found that when 1,1-diphenyl-2-chloroethylene is reacted with benzene in the presence of aluminum chloride, the same condensation products are formed as in the reaction of trichloroethylene with benzene.

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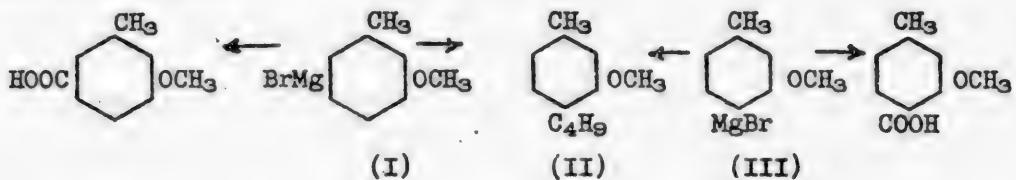
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ISOMERIZATION IN ORGANOMAGNESIUM SYNTHESIS. II

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Organic Chemistry, USSR Academy of Sciences

In 1937 the author [1] described the first observed instance of isomerization in organomagnesium synthesis, involving the migration of a tert-butyl group in the aromatic ring, viz: when tert-butyl bromide or iodide is reacted with the organomagnesium derivative of 5-bromo-3-methoxy-1-methylbenzene (I), instead of getting the expected "normal" reaction product - 5-tert-butyl-3-methoxy-1-methylbenzene - we found we had synthesized 4-tert-butyl-3-methoxy-1-methylbenzene (II), with a m.p. of 23-24°, which had been previously synthesized in two ways: 1) from the organomagnesium derivative of 4-bromo-3-methoxy-1-methylbenzene (III) and tert-butyl bromide; and 2) by the action of isobutylene or tert-butyl chloride upon 3-methoxy-1-methylbenzene in the presence of AlCl_3 .

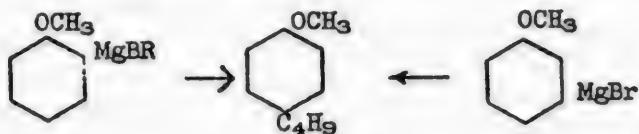


On the other hand, it is of interest to note that the reaction of the organomagnesium derivative of 6-bromo-3-methoxy-1-methylbenzene with tert-butyl iodide is not accompanied by the migration of the tert-butyl group, but results in the synthesis of 6-tert-butyl-3-methoxy-1-methylbenzene [3].

Recently we have been able to study this phenomenon more closely, using the bromine derivatives of anisole as our examples. We obtained the following results: the reaction of the organomagnesium derivative of m-bromoanisole with dimethyl sulfate, n-butyl iodide, allyl iodide, and carbon dioxide was unaccompanied by isomerization, the respective m-methylanisole, m-n-butylandisole, m-allylanisole, and m-methoxybenzoic acid being formed. Similarly, the reaction of the organomagnesium derivative of o-bromoanisole with dimethyl sulfate, n-butyl iodide, benzyl chloride, and carbon dioxide yielded ortho substituted anisoles: o-methylanisole, o-n-butylandisole, o-benzylanisole, and o-methoxybenzoic acid.

On the other hand, the reaction of organomagnesium derivatives of meta and ortho bromoanisole with tert-butyl iodide is accompanied by the migration

of the tert-butyl group to the para position, resulting in the formation of a single product - p-tert-butylanisole:



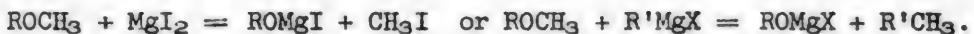
Thus, it has been demonstrated that when various compounds containing a mobile halogen atom are employed (benzyl chloride, allyl iodide) migration is observed only with a tert-butyl halide, i.e., this phenomenon is specific for the tert-butyl group. Moreover, the migration is toward the position determined by the orienting influence of the substituent. Thus, anisole and tert-butyl alcohol in the presence of H_3PO_4 yield p-tert-butylanisole [4], whereas m-cresol yields 4-tert-butyl-3-hydroxy-1-methylbenzene [5].

We were unable to isolate the "normal" reaction products. Isomerization is apparently almost 100%. An indirect proof of their formation, however, is the fact that the crude product of the nitration of tert-butylanisole, synthesized from m-anisyl-magnesium bromide

and tert-butyl iodide has a strong musk odor. As we see it, this is due to the presence of traces of 4,6-dinitro-3-tert-butyl-anisole, not described in the literature, which should have a musky odor in our opinion. Experiment shows [1] that the synthesis of such, as yet unknown, derivatives of the m-tert-butylphenols is a difficult task.

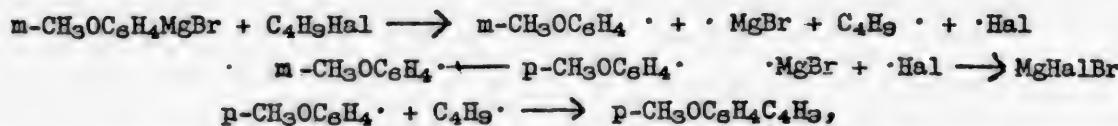
Ortho and, particularly, meta bromoanisole usually react only with activated magnesium. Instead of activating magnesium, we successfully used an ester of silicic acid, which catalyzes the reaction as K. Andrianov and O. Gribanova has shown [6]. When 2-3 drops of $(C_2H_5O)_4Si$ and a tiny crystal of iodine are added, the reaction with magnesium often sets in without preheating.

When $CH_3OC_6H_4MgBr$ or $CH_3O(CH_3)C_6H_3MgBr$ are reacted with alkyl halides, many by-products are obtained, the most important of which is almost always anisole or methoxytoluene in quantities of 15-25% of the theoretical. Formation of these latter cannot be explained by a simple hypothesis - the decomposition of the unreacted organomagnesium compound by water - since in every instance the reaction mixture was heated until a sample of the solution failed to exhibit the sensitive reaction with Michler's ketone [7]. Failure to obtain color indicates the absence of an organomagnesium compound. In addition to the anisole and methoxytoluene, we also get phenol derivatives (3-5%), probably as follows:



The reactions involved in the migration of the tert-butyl group are characterized by extremely great rapidity. The reaction with tert-butyl iodide does not begin in an ether solution, but after the ether has been driven off, a violent reaction sets in, which is over in 20-30 seconds. Gaseous substances (up to 0.25 mole per mole of the tert-butyl halide) are formed, and frequently free halides.

It seems to us that these facts justify the representation of the principal stages of the reaction by the following equations:

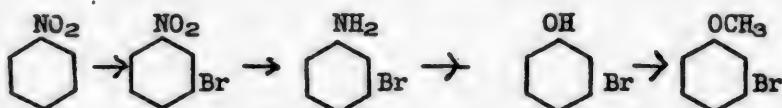


the formation of anisole and methoxytoluene being probably due to disproportionation in accordance with:



EXPERIMENTAL

The initial ortho bromoanisole was prepared from ortho anisidine by a diazo reaction [9], the meta bromoanisole being prepared by the following method [10]:



In all our experiments the solution of the organomagnesium derivative was prepared from 18.7 g (0.1 mole) of the bromoanisole, 3 g of Mg, and 80 ml of absolute ether with 2-3 drops of $(\text{C}_2\text{H}_5\text{C})_4\text{Si}$ and a tiny crystal of iodine added. The solution obtained was combined with an excess of magnesium. Heating with the alkyl chloride was continued until the Michler's ketone reaction was negative. After the reaction mass had been decomposed with ice and hydrochloric acid, the ether solution was washed with an alkaline solution to remove the phenols. The reaction products were carefully fractionated with a herringbone dephlegmator.

Ortho anisylmagnesium bromide and CO_2 . Synthesized: ortho methoxybenzoic acid, with a m.p. of 99-100° from methanol. According to Graebe [11], the acid fuses at 98.5°.

Meta anisylmagnesium bromide and CO_2 . Synthesized: meta methoxybenzoic acid, with a m.p. of 104-105° (from water). The literature gives the melting point of this acid as 104-105°, 106-107°, and 110° [12].

Ortho anisylmagnesium bromide and dimethyl sulfate. A solution of the organomagnesium derivative is added drop by drop at 3-4°, with constant stirring, to a solution of dimethyl sulfate (0.2 mole) in 70 ml of absolute ether. The mixture was heated over a water bath for 3 hours.

- 1) 151-153°, 2 g anisole. M.p. of trinitroanisole is 59°.
- 2) 169-171°, 4.6 g o-methylanisole. Oxidation with KMnO_4 (heating over water bath) yielded the acid with a m.p. of 99-100°. A mixed sample with ortho methoxybenzoic acid exhibited no depression.

Meta anisylmagnesium bromide and dimethyl sulfate. Conditions as in foregoing experiment.

- 1) 151-153°, 1.7 g anisole.
- 2) 171-173°, 4.4 g m-methylanisole. Oxidation with KMnO_4 yielded the

acid with a m.p. of 104-105°. A mixed test sample with meta methoxybenzoic acid fused at 104-105°.

Meta anisylmagnesium bromide and tert-butyl iodide. The reaction does not start in an ether solution. After the ether had been driven off on a boiling water bath, tert-butyl iodide was added to the cooled residue. Within a minute a violent reaction set in, lasting half a minute. 600 ml of gas (0°, 760 mm) was collected, corresponding to 1/4 mole per mole of the iodide. The gas decolors bromine water. At 2 mm:

- 1) 35-37°, 1.8 g anisol; m.p. of trinitroanisole is 59°.
- 2) 70-72°, 4.2 g para tert-butylanisole.
- 3) 86-87°, 1.2 g.

When the second fraction was heated together with HI (b.p. 125-127°) in a flask equipped with a reflux condenser, para tert-butylphenol, with a m.p. of 99-100° (from lignoin) is synthesized in no more than one hour. A mixed test sample with pure para tert-butylphenol, prepared from phenol and tert-butyl alcohol (H_3PO_4) [4], fuses at 99-100°. Nitration of 1 g of the second fraction, dissolved in 10 g of acetic anhydride, by 4.1 ml of HNO_3 (sp. gr 1.5) at 0° yielded a crystalline substance, with a strong odor of musk; crystallization from methanol, however, yielded light-yellow, platelike, odorless needles with a m.p. of 101-102°. A mixed test sample with standard 2,6-dinitro-4-tert-butylanisole (from para tert-butylphenol after methylation and nitration) exhibited no depression. The yield was 78% of the theoretical. We were unable to isolate the substance with a musky odor.

Ortho anisylmagnesium bromide and tert-butyl iodide. The reaction does not take place when they are heated together in an ether solution. As the driving off of the ether over a water bath draws to a close, a violent reaction suddenly sets in, lasting 20-25 seconds. At 2 mm:

- 1) 35-37°, 3.1 g anisole.
- 2) 70-72°, 5.1 g para tert-butylanisole.

Reaction with HI yielded para tert-butylphenol, with a m.p. of 99-100°, which was identical with that synthesized previously. Nitration of 1 g of the second fraction yielded 0.9 g of a crystalline substance that had no odor of musk. M.p 101-102° (from methanol). A mixed test sample with standard 2,6-dinitro-4-tert-butylanisole and with the substance synthesized in the previous experiment exhibited no depression.

Meta anisylmagnesium bromide and n-butyl iodide. The ether was driven off from the solution, the iodide was added, and the mixture was heated, first for 6 hours over a boiling water bath, and then for 5 hours at 140-145°. At 11 mm:

- 1) Up to 99°: 2 drops.
- 2) 99-100°, 3.0 g - meta n-butylanisole.

3.570 mg substance: 10.515 mg CO_2 ; 3.140 mg H_2O .

Found %: C 80.41; H 9.85.

$C_{11}H_{16}O$. Calculated %: C 80.49; H 9.76.

1 g of the synthesized meta n-butyylanisole was oxidized with a 3% solution of KMnO₄ (7.7 g) at 100°. This yielded an acid with a m.p. of 104-105°. A mixed test sample with meta methoxybenzoic acid exhibited no depression.

Ortho anisylmagnesium bromide and n-butyl iodide. Heating for 7 hours at 145-150°.

- 1) 150-152°, 1.4 g - anisole.
- 2) 221-223°, 2.1 g - ortho n-butyylanisole.
- 3) At 5 mm 110-160°.

Analysis of the second fraction:

3.920 mg substance; 11.510 mg CO₂; 3.395 mg H₂O.

Found %: C 80.35; H 9.71.

C₁₁H₁₆O. Calculated %: C 80.49; H 9.76.

Oxidation with KMnO₄ yielded an acid with a m.p. of 98-99°. A mixed test sample with ortho methoxybenzoic acid fused at the same temperature.

The third fraction crystallized upon standing. The crystals, with the oil pressed out, crystallized from methanol. Tiny colorless needles with a m.p. of 153-154°.

Ullmann [13] gives 154° as the m.p. of o,o-dianisyl.

Meta anisylmagnesium bromide and allyl iodide. Allyl iodide was added to the ether solution. The ether began to boil almost immediately. The velocity of the reaction was regulated by immersing the flask in cold water. The end of the reaction was followed by heating over a water bath for 1.5 hours. At 2 mm:

- 1) Up to 70°, 2 drops.
- 2) 70-71°, 8.5 g - meta allylanisole.

Yield: 58% of the theoretical.

A colorless liquid with a characteristic odor, d₂₀²⁰ 0.9780; n_D²⁰ 1.5245.

4.800 mg substance: 14.142 mg CO₂; 3.475 mg H₂O.

4.400 mg substance: 12.960 mg CO₂; 3.125 mg H₂O.

Found %: C 80.40, 80.38; H 8.10, 7.94.

C₁₀H₁₂O. Calculated %: C 81.08; H 8.11.

When 1 g of the substance was oxidized in the cold with a 3% solution of KMnO₄ (6 g), about 1/3 of the permanganate was reduced rapidly. The mixture was then heated over a water bath for 4 hours. The acid obtained was twice recrystallized from water. M.p. 104-105°. A mixed test sample with meta methoxybenzoic acid exhibited no depression.

Ortho anisylmagnesium bromide and benzyl chloride. The substances do not react together in an ether solution. As the driving off of the ether over a water bath drew to a close, a brief and violent reaction ensued. At 3 mm the following fractions were collected:

- 1) 123-124°, 9.3 g.
- 2) 193-196°, 1.3 g.

The first fraction crystallized when it was chilled with ice. The crystals were put through a filter press and then recrystallized from methanol. The well-shaped, almost square, thick platelets had a m.p. of 29-30°. A mixed test sample with ortho benzylanisole, prepared by Claisen's method [14] from sodium phenolate and benzyl chloride with ensuing methylation, which had a m.p. of 30°, exhibited no depression.

The 193-196° fraction is identifiable as dibenzylanisole by its analytical data and boiling point.

4.456 mg substance: 14.350 mg CO₂; 2.706 mg H₂O.
5.951 mg substance: 19.185 mg CO₂; 3.739 mg H₂O.
Found %: C 87.80, 87.91; H 6.79, 7.03.
C₂₁H₂₀O. Calculated %: C 88.15; H 7.01.

SUMMARY

1. It was shown that when the ortho and meta anisylmagnesium bromides are reacted with tert-butyl iodide, the tert-butyl group migrates to the methoxyl group at the para position. This property is specific for tert-butyl halide. Other alkyl halides yield "normal" reaction products, the respective ortho- and meta-substituted anisoles.

2. The reaction mechanism is suggested.

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STERIC HINDRANCES IN ORGANOMAGNESIUM REACTIONS

VIII. THE SYNTHESIS OF α -OXYKETONES

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In 1902 N. D. Zelinsky [1] demonstrated, using the reaction of methyl magnesium iodide with diacetyl, that α -diketones react with organomagnesium compounds quite actively, forming pinacones. Subsequently, this course of the reaction between the foregoing substances was confirmed by other researchers. Using this same reaction, Pace [2] synthesized methylethyl- and methylpropyl-pinacone, Grignard and Vignon [3] synthesized dimethylcycloheptanediol, and Johlin [4] synthesized methylphenylpinacone. Using this same method, Yushchenko [5] synthesized 4,5-dimethyloctadiene-1,7-diol-4,5, and 4,5-diphenyloctadiene-1,7-diol-4,5. Benzyl [6] and anisyl [7] react likewise. Fuson and Robertson [8], investigating the reaction of tert-butylmesityl diketone with methylmagnesium iodide, demonstrated that the more complex α -diketones also react similarly, and that the addition of methylmagnesium iodide is attached to each carbonyl group at the 1,2 position.

It follows from the results of these investigations that both carbonyl groups react extremely reactively in the α -diketones, which is why pinacones are formed with good yields when enough of the organomagnesium compound is present. If the quantity of the latter is insufficient, a mixture of pinacones and α -oxyketones is formed as a rule. Bearing this in mind, Diels and Johlin [9] protected one carbonyl group during the synthesis of α -oxyketones from α -diketones and organo magnesium compounds, converting it into a methylphenylhydrazone; since the latter hardly reacts at all with organomagnesium compounds, the reactions result in the synthesis of methylphenylhydrazones of the α -oxyketones, which split off the hydrazine group when boiled with water and benzaldehyde, thus being transformed into α -oxyketones. This method was used to synthesize trimethyl-, dimethylethyl-, and dimethylphenyl ketols. Only Acree [10] succeeded in synthesizing phenylbenzoin from benzyl and phenylmagnesium bromide by carrying out the reaction under special conditions.

Continuing our research on the effect of steric hindrances upon the course of organomagnesium reactions, we set as the object of the present paper the investigation of the possibility of synthesizing α -oxyketones by direct reaction from a highly active α -diketone - diacetyl - and organomagnesium compounds.

Research indicated that such syntheses are quite feasible, owing to the steric hindrances created by the ortho position of the substituents in aryl magnesium halides, and in these reactions only one of the carbonyl groups reacts, α -oxyketones being formed. But to make the latter the sole products of

the reaction, without any trace of pinacones, the reaction conditions must be changed somewhat, viz: the sequence in which the reacting components are mixed together must be altered (an equimolecular quantity of the Grignard reagent is added to an ether solution of the α -diketone), and chilling must be employed at the instance of mixing.

When a diortho-substituted aryl magnesium halide, namely, mesitylmagnesium bromide, is reacted with an equimolecular quantity of diacetyl under the specified conditions, we get methyl-(2,4,6-trimethylphenyl)-acetylcarbinol (I) as the sole reaction product, with a yield of about 25% (Experiment 1).

Monoortho-substituted toluenemagnesium halides react in the same way. When ortho toluenemagnesium bromide is reacted with an equimolecular quantity of diacetyl, we again get methyl- α -tolylacetylcarbinol (II) as the sole product, with a yield of 42% (Experiment 2).

A more highly branched alkyl at the ortho position in an aryl magnesium bromide, say, an isopropyl, reduces the yield of the α -oxyketone only slightly below that obtained from α -tolylmagnesium bromide. For example, 3-cymylmagnesium bromide reacts with an equimolecular quantity of diacetyl to form methyl-(3-methyl-6-isopropylphenyl)-acetylcarbinol (III), with a yield of 25% (Experiment 3).

As we know, naphthalene possesses a number of characteristic properties that distinguish it from the benzene ring. The principal one of these characteristics is the higher reactivity of the carbon atom at the alpha position. Moreover, the second ring in naphthalene may be looked upon as one ortho substituent that establishes a steric hindrance. The combination of these two factors governs the course of the reaction; it may, therefore, be expected that α -naphthylmagnesium bromide will react with diacetyl under the specified conditions to form an α -oxyketone, but the amount of the ketol produced will be greater than with α -tolylmagnesium bromide, owing to the activity of the alpha carbon. Research confirmed this conjecture.

When α -naphthylmagnesium bromide reacts with an equimolecular quantity of diacetyl, there is formed, again as the sole product, methyl- α -naphthylacetylcarbinol (IV), with a yield of 45% (Experiment 4).

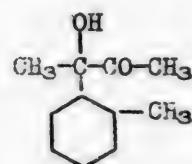
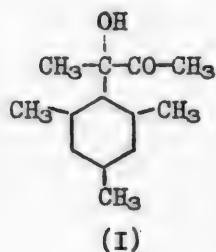
The results of these reactions are changed when aryl magnesium halides with an unsubstituted ortho position are used. In these cases we get a mixture of α -oxyketones and pinacones, even when the specified conditions are maintained. Reacting phenylmagnesium bromide with an equimolecular quantity of diacetyl yields as the principal product methylphenylacetylcarbinol (V) with a yield of 30%, but 13% of a higher boiling product, which is probably symm. methylphenyl pinacone, is also formed (Experiment 5).

The results obtained are set forth in the following table to provide a comparison of the yields of α -oxyketones as a function of the structure of the organomagnesium compounds. (Cf. Table on page 671.)

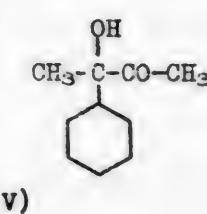
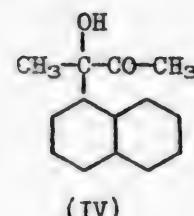
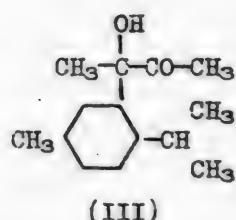
It follows from what has been said, therefore, that the α -oxyketones cannot be synthesized by the reaction of organomagnesium compounds with α -diketones only in the case of a fairly small group of unbranched organomagnesium compounds of low molecular weight; even when used in equimolecular proportions with respect

Test No.	Reagents (1:1 ratio)	Name of synthesized α -ketol	Yield in %	Property					
				Boiling point	d_{4}^{20}	n_{D}^{20}	MR _D		M.p. of phenylhydrazone
Found	computed								
1	Mesitylmagnesium bromide + diacetyl	Methyl-(2,4,6-trimethylphenyl)-acetylcarbinol	24	113-115° (2 mm)	1.0344	1.5165	60.28	60.17	174-175°
2	<i>o</i> -Tolylmagnesium bromide + diacetyl	Methyl- <i>o</i> -tolyl-acetylcarbinol	42	105-106° (2.5 mm)	1.0593	1.5235	51.36	50.93	135-137°
3	3-Cymylmagnesium bromide + diacetyl	Methyl-(3-methyl-6-isopropylphenyl)-acetylcarbinol	25	127-130° (7 mm)	1.0156	1.5135	65.16	64.79	-
4	α -Naphthylmagnesium bromide + diacetyl	Methyl- α -naphthylacetylcarbinol.	45	155-156° (3 mm)	-	-	-	-	-
5	Phenylmagnesium bromide + diacetyl	Methylphenyl-acetylcarbinol	30	88-90° (2 mm)	1.0915	1.5340	46.70	46.32	-

to the α -diketone, these latter form a mixture of α -oxyketones and pinacones.



(II)



Another, much larger, group of organomagnesium compounds, which set up steric hindrances (diortho- and monoortho-substituted aryl magnesium halides, and, probably, branched alkyl magnesium halides) form an α -oxyketone as the sole reaction product, without any trace of a pinacone, when reacted with equimolecular quantities of α -diketones under the conditions specified above.

EXPERIMENTAL

1. Reaction of Mesitylmagnesium Bromide with Diacetyl (1:1 Ratio)

We used 50 g (0.25 mole) of mesitylene bromide, 7 g of magnesium, and 21.5 g (0.25 mole) of diacetyl.

An ether solution of the mesitylmagnesium bromide was poured into an ether solution of the diacetyl, with constant chilling and stirring. A yellow precipitate was formed at once, which first turned pink and then orange upon heating. After mixing was complete, the reaction mixture was heated for 10 hours and decomposed with water and 10% acetic acid. The ether layer was separated from the aqueous layer and washed with a 10% soda solution and then with water. After the ether solution was dried with anhydrous sodium sulfate, the ether was driven off over a water bath, and the residue was distilled in vacuum to avoid dehydration.

Fraction I: B.p. up to 110° (6 mm)	16.3 g.
Fraction II: B.p. 110-175° (6 mm)	15.8 g
Residue	2.0 g

Redistillation of Fraction II yielded 12.4 g (24%) of methylmesityl-acetylcarbinol, with a b.p. of 113-115° (2 mm). This α -oxyketone is highly soluble in petroleum ether, alcohol, acetone, and benzene. It is cleaved by a 50% aqueous alcohol.

0.1171 g substance:	0.3229 g CO ₂ ; 0.0895 g H ₂ O.
0.1033 g substance:	0.2856 g CO ₂ ; 0.0810 g H ₂ O.
	Found %: C 75.40, 75.40; H 8.55, 8.77.
C ₁₃ H ₁₈ O ₂ .	Calculated %: C 75.69, H 8.79.
0.1527 g substance:	18.6 ml CH ₄ (14°, 750 mm)
	Found %: OH 8.64.
C ₁₃ H ₁₈ O ₂ .	Calculated %: OH 8.25.
	d ₄ ²⁰ 1.0344; n _D ²⁰ 1.5165; M _R _D 60.28.
	Calculated M _R _D 60.17.

To synthesize the phenylhydrazone of methylmesitylacetylcarbinol, a weighed amount of the α -oxyketone was dissolved in glacial acetic acid, and a slight excess of phenylhydrazine was added to the solution. After standing for four days in a cold place, the mixture crystallized; the phenylhydrazone was filtered out and purified by recrystallization from alcohol. M.p. 174-175°.

0.1162 g substance:	consumed 8 ml 0.1N H ₂ SO ₄ *
	Found %: N 9.70.
C ₁₉ H ₂₄ ON ₂ .	Calculated %: N 9.45.
0.1293 g substance:	20.5 ml CH ₄ (11°, 777 mm).
	Found %: H 0.70.
C ₁₉ H ₂₄ ON ₂ .	Calculated %: H 0.68.

* Nitrogen was determined by the Kjeldahl method, modified appropriately for the hydrazone by Milbauer [11].

Neither methylmesitylacetylcarbinol nor its phenylhydrazone have been described in the literature.

2. Reaction of o-Tolylmagnesium Bromide with Diacetyl (1:1 ratio)

Initial substances: 34.2 g of o-toluene bromide (0.2 mole), 5.8 g of magnesium, and 17.2 g of diacetyl (0.2 mole). As in the preceding experiment, an ether solution of the o-tolylmagnesium bromide was added to an ether solution of the diacetyl. After the usual decomposition of the organomagnesium coordination compound, the product was distilled in vacuum (avoiding partial dehydration).

Fraction I: b.p. up to 90° (4 mm).

Fraction II: b.p.	90-145° (4 mm)	18.0 g
	Residue	2.0 g

Redistillation of Fraction II yielded 15.0 g (42.0% of methyl-o-tolylacetylcarbinol, with a b.p. of 105-106° (2.5 mm)).

d_4^{20} 1.0593; n_D^{20} 1.5235; MR_D 51.36; calculated MR_D 50.93.

0.1223 g substance: 0.3311 g CO_2 ; 0.0854 g H_2O .

0.0980 g substance: 0.2663 g CO_2 ; 0.0707 g H_2O .

Found %: C 73.87, 74.15; H 7.81, 8.07.

$C_{11}H_{14}O_2$. Calculated %: C 74.12; H 7.92.

0.1636 g substance: 20.8 ml CH_4 (14°, 750 mm).

Found %: OH 9.04.

$C_{11}H_{14}O_2$. Calculated %: OH 9.55.

When reacted with phenylhydrazine under conditions of Experiment 1, methyl-o-tolylacetylcarbinol forms the phenylhydrazone, with a m.p. of 135-137° (from alcohol).

0.1405 g substance: consumed 10.2 mg 0.1N H_2SO_4 .

Found %: N 10.20

$C_{17}H_{20}ON_2$. Calculated %: N 10.44.

0.1348 g substance: 24 ml CH_4 (11°, 777 mm).

Found %: H 0.80.

$C_{17}H_{20}ON_2$. Calculated %: H 0.79.

Neither methyl-o-tolylacetylcarbinol nor its phenylhydrazone is mentioned in the literature.

3. Reaction of 3-Cymylmagnesium Bromide With Diacetyl (1:1 Ratio)

Initial substances: 43 g (0.2 mole) of 3-cymyl bromide, 5.8 g of magnesium, and 17.2 g (0.2 mole) of diacetyl.

The reaction conditions were the same as in Experiment 1.

Fraction I: b.p. up to 110° (7 mm) 18.0 g.

Fraction II: b.p. 110-150° (7 mm) 14.0 g.

Residue 2.0 g.

Redistillation of Fraction II yielded 11 g (25%) of methyl-(3-methyl-6-isopropylphenyl)-acetylcarbinol, with a b.p. of 127-130° (7. mm).

d_4^{20} 1.0156; n_D^{20} 1.5135; M_R_D 65.15; Calculated M_R_D 64.79.

0.1186 g substance: 0.3320 g CO_2 ; 0.0989 g H_2O .

Found %: C 76.39; H 9.33.

$C_{14}H_{20}O_2$. Calculated %: C 76.32; H 9.15.

0.1494 g substance: 17 ml CH_4 (14° , 750 mm)

Found %: OH 8.0..

$C_{14}H_{20}O_2$. Calculated %: OH 7.7.

This α -oxyketone is not described in the literature.

4. Reaction of α -Naphthylmagnesium Bromide with Diacetyl (1:1 Ratio)

Initial substances: 41.4 g (0.2 mole) of α -naphthalene bromide, 5.8 g of magnesium, and 17.2 g (0.2 mole) of diacetyl.

The reaction conditions were the same as in Experiment 1.

Fraction I: b.p. up to 160° (5 mm) 9.0 g,

Fraction II: b.p. $160-190^\circ$ (5 mm) 24.0 g.

Residue 3.0 g.

Redistillation of Fraction II yielded 21.0 g (45%) of methyl- α -naphthyl-acetylcarbinol, with a b.p. of $155-156^\circ$ (3 mm). This ketone crystallizes out of an aqueous alcohol upon chilling as a monohydrate.

0.1160 g substance: 0.3084 g CO_2 ; 0.0734 g H_2O .

Found %: C 72.55; H 7.08.

$C_{14}H_{14}O_2 \cdot H_2O$. Calculated %: C 72.39; H 6.95.

0.1080 g substance: 33 ml CH_4 (14° , 750 mm)

Found %: OH 21.67.

$C_{14}H_{14}O_2 \cdot H_2O$. Calculated %: OH 21.9.

When the crystals of the methyl- α -naphthylacetylecarbinol monohydrate are dessicated in vacuum, they lose part of their water and are converted into a liquid with the b.p. of $155-156^\circ$ (3 mm) given above for methyl- α -naphthyl-acetylcarbinol.

0.1249 g substance: 0.3578 g CO_2 ; 0.0748 H_2O .

Found %: C 78.18; H 6.70.

$C_{14}H_{14}O_2$. Calculated %: C 78.48; H 6.59.

This α -oxyketone is not described in the literature.

5. Reaction of Phenylmagnesium Bromide with Diacetyl (1:1 Ratio)

The reaction was effected with 31.4 g (0.2 mole) of bromobenzene, 5.8 g of magnesium, and 17.2 g (0.2 mole) of diacetyl.

The reaction conditions were the same as in Experiment 1.

Fraction I: b.p. up to 145° (13 mm) 14.0 g.

Fraction II: b.p. $125-170^\circ$ (4 mm) 3.0 g.

Residue 3.0 g.

Repeated redistillation of Fraction I yielded 10.5 g (30%) of methylphenylcarbinol, with a b.p. of $88-90^\circ$ (2 mm); d_4^{20} 1.0915; n_D^{20} 1.5340; M_R_D 46.70; calc. M_R_D 46.32.

0.1091 g substance: 0.2918 g CO₂; 0.0718 g H₂O.
Found %: C 72.97; H 7.36.
C₁₀H₁₂O₂. Calculated %: C 73.14; H 7.37.
0.1518 g substance: 22.2 ml CH₄ (14°, 750 mm).
Found %: OH 10.47
C₁₀H₁₂O₂. Calculated %: OH 10.1.

The literature gives 122-123° (8 mm) as the boiling point of this ketone [8].

We were unable to effect the crystallization of Fraction II (125-170° at 4 mm), which was in all probability a mixture of symm. methylphenylpinacone and products of the latter's dehydration, and in view of the negligible quantity of this fraction available, we made no further investigation of it.

SUMMARY

1. Synthesis of α-oxyketones by the action of organomagnesium compounds upon α-diketones is impossible only when a comparatively small group of unbranched organomagnesium compounds of low molecular weight is used; these compounds form a mixture of α-oxyketones and pinacones, even when they are used in equimolecular proportions with the α-diketones.

Another, much larger, group of organomagnesium compounds (diortho- and monoortho-substituted aryl magnesium halides and, probably, branched alkyl magnesium halides), when reacted with equimolecular quantities of α-diketones, form α-oxyketones if the reacting components are mixed together in reverse order. The method outlined is satisfactory for the synthesis of α-oxyketones with this group of organomagnesium compounds.

2. Four α-oxyketones hitherto unmentioned in the literature were synthesized and described.

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STERIC HINDRANCES IN ORGANOMAGNESIUM REACTIONS

IX. SYNTHESIS OF KETONES BY THE REACTION OF ACID HALIDES WITH ORGANOMAGNESIUM COMPOUNDS

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The reactions of the acid halides with organozinc compounds were first investigated by A.M. Butlerov [1], who synthesized tertiary butyl alcohol in 1864 by reacting two moles of methylzinc with one mole of acetyl chloride. Butlerov used this same reaction [2] to synthesize methyldiethyl-, propyldimethyl-, and propyldiethylcarbinol. Lastly, Butlerov [3] used the same reaction to synthesize tertiary heptyl alcohol.

A. Popov demonstrated, however, [4] that the same initial substances, but in other quantitative proportions, this reaction can be halted at an intermediate stage, the stage at which ketones are formed. Using this modification of the method, Popov synthesized a large number of aliphatic ketones. The feasibility of synthesizing ketones from acid chlorides and organozinc compounds was also proved by other researchers [5,6,7].

Grignard [8] applied this method of synthesizing the tertiary alcohols to the field of organomagnesium compounds. Like the organozinc compounds, the organomagnesium compounds form tertiary alcohols with the chlorides of monocarboxylic acids.

Organomagnesium compounds differ from organozinc compounds in that they react with acid chlorides so actively that it has been believed that it is impossible to halt this reaction at the stage in which ketones are formed. For example, in his textbook of organic chemistry, Zalkind [9] writes that "organomagnesium compounds are not suitable for this reaction since with them the reaction cannot be halted at the first stage, the reaction always continuing to the formation of the tertiary alcohol, even when the acid chloride is present in excess."

Runge, in his monograph on organomagnesium compounds [10], writes that ketones are sometimes formed alongside the tertiary alcohols under known conditions, and that "Gilman, Fothergill, and Parker, taking special precautions, synthesized benzophenone with a yield of 45% from benzoyl chloride and phenylmagnesium bromide; 32.6% of triphenylcarbinol and 10% of diphenyl were also recovered. The author recommends that organo-zinc compounds be used preferably." Several other similar examples are cited in the same monograph.

The conclusions that the reaction of organomagnesium compounds with acid chlorides yields tertiary alcohols or, at best, a mixture of tertiary alcohols and ketones, were based upon a study of these reactions with unbranched alkyl magnesium halides or phenylmagnesium bromide of relatively low molecular weight. If the investigation is expanded to cover a wider field, these conclusions may be changed.

There are two other possible courses for the reaction between organomagnesium compounds and the halides of monocarboxylic acids that might be predicted, namely: first, that the reaction come to a halt at the stage in which ketones are formed under any reaction conditions owing to steric hindrances (irrespective of the duration of heating, the quantitative proportions of the reagents, or the order in which they are mixed, but excluding, of course, the employment of high temperatures); and second, that the steric hindrances be insufficient to halt the reaction at the first stage, certain conditions being required to guide the reaction toward the formation of ketones (say, mixing the reacting components in equimolecular proportions, adding the Grignard reagent to a chilled ether solution of the acid chloride, etc.).

To check these possibilities, an investigation was undertaken of the reaction between acid chlorides and aryl magnesium halides having one or two substituents at the ortho position, and of the reaction between acid chlorides and aryl magnesium halides with unsubstituted ortho positions.

As these investigations proved, both of the hypothetically possible courses of this reaction are real.

When equimolecular quantities of benzoyl chloride and mesitylmagnesium bromide are reacted together (an ether solution of the Grignard reagent being poured into a chilled ether solution of the benzoyl chloride), phenylmesityl ketone (I) is obtained as the sole reaction product, (Experiment 1). Changing the reagent proportions (2 moles of mesitylmagnesium bromide per mole of benzoyl chloride), employing the ordinary sequence of mixing the reacting components (the solution of benzoyl chloride is added to the Grignard reagent), and heating the reaction mixture for a longer time did not affect the results. The ketone remained the sole product of the reaction.

In contrast to diortho-substituted aryl magnesium halides, the mono-ortho-substituted halides do not establish adequate steric hindrances to halt the reaction at the stage where ketones are formed. Conditions that favor this must be created, and then the ketones are again almost the only product of the reaction.

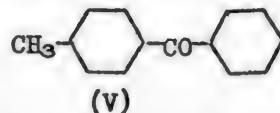
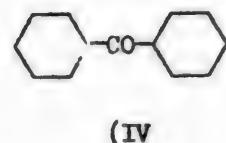
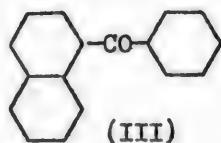
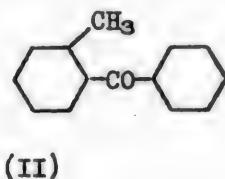
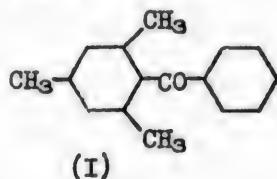
When 2 moles of o-tolylmagnesium bromide are reacted with 1 mole of benzoyl chloride, we get a mixture of phenyl-o-tolyl ketone with phenyl-di-o-tolylphenylcarbinol. But if an ether solution of an equimolecular quantity of o-tolylmagnesium bromide is added to a chilled ether solution of benzoyl chloride, the phenyl-o-tolyl ketone (II) is almost the only reaction product, as the amount of phenyl-di-o-tolylcarbinol formed is quite negligible (Experiment 2).

Thus, by using mono&ortho-substituted aryl magnesium compounds and benzoyl chloride in equimolecular proportions, we can obtain ketones as the principal reaction product under certain reaction conditions.

The same conclusion may be reached with regard to α -naphthylmagnesium bromide. When 2 moles of α -naphthylmagnesium bromide are reacted with 1 mole of benzoyl chloride, we again get a mixture of a ketone and a tertiary alcohol. But when equimolecular quantities of α -naphthylmagnesium bromide and benzoyl chloride are reacted together under certain given conditions, we get phenyl- α -naphthyl ketone (III) as the sole product of the reaction (Experiment 3). This reaction has also been investigated by Acree [11], who also obtained phenyl- α -naphthyl ketone.

Aryl magnesium halides with unsubstituted ortho positions form a mixture of a ketone and a tertiary alcohol when reacted with benzoyl chloride, even under favorable conditions. This is the conclusion that follows from the work of Gilman, Fothergill, and Parker cited above [12]; these researchers found that when phenylmagnesium bromide is reacted with benzoyl chloride a mixture of benzophenone (45%) and a tertiary alcohol is formed. We repeated this reaction, chilling the reaction mixture strongly, which enabled us to reduce the yield of the tertiary alcohol, but we could not halt the reaction altogether at the first stage. In our experiment we obtained 40% of benzophenone (IV) and 14% of the tertiary alcohol (Experiment 4).

p-Tolylmagnesium bromide, which has no ortho-substituent, to be sure, behaves somewhat singularly when reacted with benzoyl chloride, forming a ketone — phenyl-*o*-tolyl ketone (V) — as the sole reaction product under favorable conditions (Experiment 5).

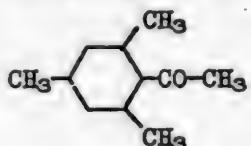


Similar results are obtained when aryl magnesium halides are reacted with acetyl chloride.

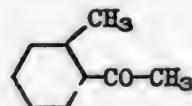
When diortho-substituted aryl magnesium halide — mesitylmagnesium bromide — is reacted with the acetyl chloride, even with the former present in excess, the sole reaction product obtained is methylmesityl ketone (VI), though with a negligible yield (Experiment 6).

The monoortho-substituted aryl magnesium halides: *o*-tolylmagnesium

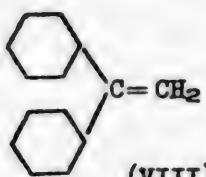
bromide and α -naphthylmagnesium bromide, form ketones with acetyl chloride only under certain conditions, specified above. With acetyl chloride, o-tolylmagnesium bromide forms methyl-o-tolyl ketone (VII) (Experiment 7) with a slight quantity of the product of the reaction's second stage: asymm. di-o-tolylethylene (VIII) (a product of the dehydration of methyl-di-o-tolylcarbinol), whereas when α -naphthylmagnesium bromide is reacted with the same acid chloride and under the same conditions we get methyl- α -naphthyl ketone (IX) (Experiment 8), again with a slight quantity of the product of the reaction's second stage, asymm. di- α -naphthylethylene (X).



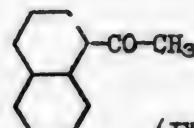
(VI)



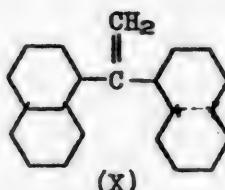
(VII)



(VIII)



(IX)



(X)

The experimental results are set forth in the accompanying table.

These results (see Table) enable us to reach the following conclusion: diortho-substituted aryl magnesium halides form ketones with the halides of monocarboxylic acids, no matter what the reaction conditions are; monoortho-substituted aryl magnesium halides form ketones only under certain conditions.

Thus, the synthesis of ketones with adequate yields from ortho-substituted aryl magnesium halides and acid halides is entirely feasible.

As for the alkyl magnesium halides, the research work already reported in the literature should suffice for the quite definite conclusion that it is also entirely feasible to synthesize ketones from branched alkyl magnesium halides and the halides of monocarboxylic acids. Whitmore and Badertteher [13] studied the reaction of acid chlorides with branched alkyl magnesium halides. Acetyl chloride forms the corresponding ketones with tert-butyl-, tert-amyl-, tert-hexyl-, and tert-heptylmagnesium chloride.

Whitmore [14] and his associates, using the reactions of tert-butylacetyl chloride with C_2H_5MgBr , $n-C_3H_7MgBr$, $n-C_4H_9MgBr$, and $n-C_5H_{11}MgBr$ as an example, found that when an ether solution of the organomagnesium compound is added to the acid chloride, ketones are formed with yields of 51, 37, 34, and 23%, respectively.

Test No.	Reagents (Ratio 1:1)	Ketone	Yield of ketone, %	Remarks
1	Mesitylmagnesiumbromide + benzoyl chloride	Phenylmesityl ketone	34	No tertiary alcohol is formed, even when an excess of the organomagnesium compound is present.
2	<i>o</i> -Tolylmagnesium bromide + benzoyl chloride	Phenyl- <i>o</i> -tolyl ketone	50	About 5% of the tertiary alcohol is formed.
3	<i>a</i> -Naphthylmagnesium bromide + benzoyl chloride	Phenyl- <i>a</i> -naphthyl ketone	69	No tertiary alcohol is formed
4	<i>p</i> -Tolylmagnesium bromide + benzoyl chloride	Phenyl- <i>p</i> -tolyl ketone	40	
5	Phenylmagnesium bromide + benzoyl chloride	Benzophenone	40	14% of tertiary alcohol is formed.
6	Mesitylmagnesium bromide + acetyl chloride	Methylmesityl ketone	10	No tertiary alcohol is formed, even when an excess of the organomagnesium compound is present.
7	<i>o</i> -Tolylmagnesium bromide + acetyl chloride	Methyl- <i>o</i> -tolyl ketone	30	14% of the product of dehydration of the tertiary alcohol: di- <i>o</i> -tolylethylene, is formed.
8	<i>a</i> -Naphthylmagnesium bromide + acetyl chloride	Methyl- <i>a</i> -naphthyl ketone	50	2.5% of di- <i>a</i> -naphthyl-ethylene is formed.

Summing up all that has been said, it may be stated that the traditional view concerning the impossibility of synthesizing ketones from organomagnesium compounds and the halides of monocarboxylic acids holds good only with respect to a comparatively small group of organomagnesium compounds of low molecular weight and acid halides, in which neither the former nor the latter component produce any steric hindrance. This conclusion does not apply to all the other groups of these compounds (diortho- and monoortho-substituted aryl magnesium halides, primary alkyl magnesium halides with long enough chains, as well as secondary and tertiary alkyl magnesium halides and the halides of tertiary acids).

If one of the reacting components (the organomagnesium compound or the acid halide) produces a steric hindrance, it is quite possible to synthesize ketones with adequate yields.

EXPERIMENTAL

1. Reaction of Mesitylmagnesium Bromide with Benzoyl Chloride (Ratio 1:1)

The reaction was carried out with 50 g of mesitylene bromide (0.25 mole), 7 g of magnesium, and 35 g (0.25 mole) of benzoyl chloride.

An ether solution of the benzoyl chloride was added to a prepared ether solution of the mesitylmagnesium bromide. The mixture was heated for 10 hours and then decomposed, first with water, and later with a 10% solution of acetic acid.

The ether solution was separated from the aqueous solution and washed, first with a 10% solution of soda and then with water, until it exhibited a neutral reaction. After the ether solution had been desiccated with sodium sulfate, the ether was driven off over a water bath, and the remaining mixture of substances was distilled in vacuum.

Fraction I:	b.p. up to 150° (15 mm)	15.6 g
Fraction II:	b.p. 150-190° (15 mm)	23.0 g
	Residue	3.0 g

Fraction II was redistilled. The major fraction, distilling at 156-162° (6 mm), totaled 19 g; a third distillation gave a b.p. of 156° (5 mm) (phenyl-mesityl ketone). Yield: 34%. The b.p. of this ketone is given in the literature [15] as 189° (17 mm).

0.1211 g substance: 0.3781 g CO₂; 0.0773 g H₂O.
Found %: C 85.20; H 7.15.
C₁₆H₁₆O. Calculated %: C 85.70; H 7.19.

The phenylmesityl ketone was reduced (Clemmensen reduction) to indicate its structure. Large transparent crystals of benzylmesitylene, with a m.p. of 36° (from alcohol) were obtained.

0.1240 g substance: 0.4149 g CO₂; 0.0964 g H₂O.
Found %: C 91.30; H 8.70.
C₁₆H₁₈. Calculated %: C 91.37; H 8.63.

The m.p. given in the literature [16] for this hydrocarbon is 36-37°.

The experiment was repeated with a change in the proportions of the reagents. 2 moles of mesitylmagnesium bromide were used per mole of benzoyl chloride. The results were the same as in the preceding experiment.

2. Reaction of o-Tolylmagnesium Bromide with Benzoyl Chloride (Ratio 1:1)

Initial substances: 57 g (0.33 mole) of o-toluene bromide, 8.5 g of magnesium, and 46.6 g (0.33 mole) of benzoyl chloride.

A prepared ether solution of o-tolylmagnesium bromide was added to an ether solution of the benzoyl chloride, chilled with ice and constantly stirred.

The very first drops changed the color of the solution markedly, and a precipitate was visible when the addition was complete. The reaction mixture was heated for 10 hours. After the usual decomposition of the magnesium coordination compound the ether was driven off, leaving behind a mixture of products, which was distilled in vacuum.

Fraction I:	b.p. up to 140° (4 mm)	15.2 g.
Fraction II:	b.p. 140-180° (4 mm)	35.2 g.
	Residue	5.0 g.

Fraction II was redistilled, yielding 33 g (50%) of phenyl-o-tolyl ketone (o-methylbenzophenone), with a b.p. of 134-137° (2 mm).

0.1102 g substance: 0.3448 g CO₂; 0.0598 g H₂O.
Found %: C 85.38; H 6.07.
C₁₄H₁₂O. Calculated %: C 85.68; H 6.17.

The b.p. of phenyl-o-tolyl ketone is given as 312-315° (735 mm) in the literature, [17].

To confirm the structure of this ketone the syn-phenyl-o-tolylketoxime was synthesized under the conditions specified by Smith [17]. The oxime exhibited a m.p. of 104-105° (from petroleum ether). Smith gives the m.p. of syn-phenyl-o-tolylketoxime at 105°.

When the amount of o-tolylmagnesium bromide was increased (2 moles of the Grignard reagent per mole of benzoyl chloride) a mixture of the ketone (phenyl-o-tolyl ketone) and a tertiary alcohol (phenyl-di-o-tolylcarbinol) was obtained.

3. Reaction of α-Naphthylmagnesium Bromide with Benzoyl Chloride (1:1 Ratio)*

The reaction conditions were the same as in the previous experiment.

An ether solution of α-naphthylmagnesium bromide, prepared from 52 g (0.25 mole) of α-naphthylene bromide and 7 g of magnesium, was slowly added, with constant stirring and chilling by ice, to an ether solution of 35 g (0.25 mole) of benzoyl chloride. When the Grignard reagent was added, the solution turned dark red.

The reaction mixture was heated for 5 hours. The mixture of substances obtained was distilled in vacuum after the ether had been driven off.

Fraction I:	b.p. up to 155° (5 mm)	8.2 g.
Fraction II:	b.p. 155-205° (5 mm)	43.0 g.
	Residue	3.0 g.

Redistillation of the 155-205° (5 mm) fraction yielded 40 g of a substance with a b.p. of 197-198° (5 mm), which crystallized and had a melting point of 75° after recrystallization from alcohol. The substance proved to be the expected phenyl-α-naphthyl ketone (yield 69%).

The m.p. of this ketone is given as 75.5° in the literature [18].

* Experiments 1, 3 and 7 were performed with the assistance of the student, G. A. Sigova.

0.1112 g substance; 0.3758 g CO₂; 0.0512 g H₂O
Found %: C 87.80; H 5.15.
C₁₇H₁₂O. Calculated %: C 87.91; H 5.21.

Clemmensen reduction of the phenyl- α -naphthyl ketone yielded a hydrocarbon - α -benzyl naphthalene, with a m.p. of 58° (from alcohol).

0.1098 g substance: 0.3758 g CO₂; 0.0627 g H₂O.
Found %: C 93.40; H 6.39.
C₁₇H₁₄. Calculated %: C 93.54; H 6.46.

The m.p. of benzyl- α -naphthalene is given as 58.5 and 59° in the literature [19].

4. Reaction of p-tolylmagnesium Bromide with Benzoyl Chloride (Ratio 1:1)

Initial substances: 43 g of p-toluene bromide (0.25 mole), 7.0 g of magnesium, and 35 g (0.25 mole) of benzoyl chloride. The reaction conditions were the same as in the previous experiment. The reaction mixture was heated for 10 hours. When the reagents were mixed together, the mixture turned a Bordeaux red, later changing to pale yellow:

Fraction I: b.p. up to 140° (6 mm).
Fraction II: b.p. 140-160° (3 mm), 21.6 g.
Residue 3.0 g.

Redistillation of the principal fraction (140-160° at 3 mm) yielded 19.6 g (40%) of phenyl-p-tolyl ketone, with a b.p. of 154-155° (3 mm), which crystallized and exhibited a m.p. of 53-54° after recrystallization from alcohol.

0.1072 g substance: 0.3360 g CO₂; 0.0586 g H₂O.
Found %: C 85.54; H 6.12.
C₁₄H₁₂O. Calculated %: C 85.68; H 6.17.

The m.p. of this ketone is given as 55° in the literature [20].

5. Reaction of Phenylmagnesium Bromide with Benzoyl Chloride (Ratio 1:1)

Used for the reaction: 31.4 g of bromobenzene (0.2 mole), 6 g of magnesium, and 28 g of benzoyl chloride (0.2 mole).

The ether solution of phenylmagnesium bromide was added to the benzoyl chloride with intensive chilling (ice + salt). The reaction mixture was set aside to stand at room temperature for 1 hour, and then decomposed in the usual manner.

Redistillation in vacuum yielded 14 g (40%) of benzophenone with a b.p. of 133-134° (3 mm).

0.113 g substance: 0.3479 g CO₂; 0.0537 g H₂O.
Found %: C 85.30; H 5.40.
C₁₃H₁₀O. Calculated %: C 85.69; H 5.53.

The oxime of benzophenone was synthesized under the conditions specified by E. Fischer [21]. The crystals of benzophenone oxime were recrystallized from a mixture of petroleum ether and acetone and exhibited a m.p. of 143-144°.

Bamberger and Seligmann give a m.p. of 143.4-144° for benzophenone oxime.

Fraction II was distilled without foaming at 160-200° (3 mm) (6 g). Upon distillation the product crystallized at once, exhibiting a m.p. of 110° after purification by recrystallization from benzene. This substance contained chlorine; it turned out to be triphenylchloromethane, for which Gomberg [23] gives a m.p. of 108-112°. A mixed test sample with triphenylchloromethane prepared from benzene and carbon tetrachloride in the presence of aluminum chloride and purified by high-vacuum distillation exhibited no depression of the melting point. The formation of triphenylchloromethane is due to the reaction of the triphenylcarbinol with the excess benzoyl chloride. Yield: 14%.

6. Reaction of Mesitylmagnesium Bromide with Acetyl Chloride

(1:1 ratio)

Initial substances: 40 g of mesitylene bromide (0.2 mole), 5.5 g of magnesium, and 15.7 g (0.2 mole) of benzoyl chloride.

An ether solution of the acetyl chloride was added to an ether solution of the mesitylmagnesium bromide, with mechanical stirring. When these substances were mixed together, the solution turned dark red, later changing to yellow. The reaction mixture was heated for 10 hours with mechanical stirring; the stirring was stopped 3 hours after the commencement of heating, owing to the high viscosity of the product. After the usual decomposition of the magnesium co-ordination compound, the mixture of substances was distilled in vacuum, yielding a fraction consisting of 3.5 g (10%) of methylmesityl ketone, with a b.p. of 99-105° (7 mm). No higher-boiling products were found.

This ketone was immediately reduced to a hydrocarbon (by the Clemmensen reduction) without further investigation. After purification, the ethylmesitylene exhibited a b.p. of 207-209° (750 mm).

0.1197 g substance: 0.3902 g CO₂; 0.1174 g H₂O.

Found %: C 88.95; H 10.98.

C₁₁H₁₆. Calculated %: C 89.12; H 10.88.

Klaces [24,25] gives the b.p. of ethylmesitylene as 208-210° and 207-208°.

7. Reaction of o-Tolylmagnesium Bromide with Acetyl Chloride

(1:1 Ratio)

Used in the reaction: 114 g of o-toluene bromide (2/3 mole), 17 g of magnesium, and 52 g of acetyl chloride (2/3 mole).

The ether solution of o-tolylmagnesium bromide was added a drop at a time, with chilling and mechanical stirring, to an ether solution of the acetyl chloride. The precipitate that formed was white, and then yellow, turning green upon heating. The mixture was heated for 10 hours, after which it was decomposed in the usual manner. The mixture of substances was then distilled in vacuum.

Fraction I:	b.p. up to 95° (20 mm).	
Fraction II:	b.p. 95-130° (20 mm)	28 g.
Fraction III:	b.p. 125-160° (4 mm)	12 g.
	Residue	2 g.

Fraction II was subjected to redistillation, yielding 26 g of methyl-*o*-tolyl ketone, with a b.p. of 68-69° (3 mm). Yield: 30%.

0.1309 g substance: 0.3850 g CO₂; 0.0866 g H₂O.

Found %: C 80.26; H 7.40.

C₉H₁₀O. Calculated %: C 80.56; H 7.51.

The boiling point of this ketone is given as 216 and 79° (5 mm) in the literature [26,27].

Clemmensen reduction of this ketone yielded a hydrocarbon with a b.p. of 164-165° (762 mm) (2-ethyltoluene).

0.1213 g substance: 0.3988 g CO₂; 0.1085 g H₂O.

Found %: C 89.72; H 10.01.

C₉H₁₂. Calculated %: C 89.93; H 10.07.

Eisenlohr and Schulz [28] give the b.p. of 163.7-163.9° (752 mm) for 2-ethyltoluene.

Fraction III was also redistilled. The hydrocarbon α,α -di-*o*-tolylethylene was synthesized with a yield of 10 g (14%), a b.p. of 124-126° (3.5 mm), and n_D²⁰ 1.5852; it is formed by the dehydration of a tertiary carbinol (methyl-di-*o*-tolylcarbinol).

0.1176 g substance: 0.3965 g CO₂; 0.0801 g H₂O.

Found %: C 92.01; H 7.62.

C₁₆H₁₆. Calculated %: C 92.25; H 7.75.

According to the literature [29], α,α -di-*o*-tolylethylene has a b.p. of 125-127° (4 mm) and n_D²⁰ 1.5854.

8. Reaction of α -Naphthylmagnesium Bromide with Acetyl Chloride (1:1 Ratio)

Used in the reaction: 52 g (0.25 mole) of α -bromonaphthalene, 7 g of magnesium, and 19.5 g (0.25 mole) of acetyl chloride. As in the preceding experiment, the ether solution of the organomagnesium compound (α -naphthylmagnesium bromide) was slowly added, with chilling and mechanical stirring, to an ether solution of the acetyl chloride, after which the mixture was heated for 10 hours and then decomposed.

Fraction I: b.p. up to 120° (3 mm) 12.2 g.

Fraction II: b.p. 120-160° (3 mm) 24.0 g.

Fraction III: b.p. 160-240° (3 mm) 3.5 g.

Redistillation of Fraction II yielded 21 g of methyl- α -naphthyl ketone (acetonaphthone), with a b.p. of 122-124° (3 mm). Yield: 50%.

0.1293 g substance: 0.4005 g CO₂; 0.0694 g H₂O.

Found %: C 84.52; H 6.01.

C₁₂H₁₀O. Calculated %: C 84.68; H 5.92.

The ketone was converted into an oxime by heating for an hour with hydroxylamine hydrochloride, dissolved in aqueous alcohol, and alkali. M.p. of the oxime 136° (from dilute alcohol). According to Roussel [30], this ketone has a b.p. of 166-167° (12 mm), and the ketone's oxime has a m.p. of 135-136°.

Fraction III (160-240° at 3 mm) crystallized; it was recrystallized from a mixture of alcohol and acetone. The crystals had a m.p. of 106-107° (1,1-di- α -naphthylethylene). Yield: 2.5%.

0.1047 g substance: 0.3615 g CO₂; 0.0537 g H₂O.
0.1147 g substance: 0.3956 g CO₂; 0.0559 g H₂O.
Found %: C 94.22, 94.12; H 5.74, 5.70.
C₂₂H₁₆. Calculated %: C 94.25; H 5.75.

According to the literature [31], this hydrocarbon has a m.p. of 107°.

SUMMARY

1. The established opinion that it is impossible to synthesize ketones from organomagnesium compounds and acid halides of monocarboxylic acids is correct only with respect to a relatively small group of organomagnesium compounds and acid halides of low molecular weight, neither the former nor latter components causing any steric hindrances. This conclusion is not applicable to all other groups of these compounds.

If the position of groups in one of the reacting components causes steric retardation to appear, the synthesis of ketones by means of the foregoing reaction is entirely possible.

2. Diortho-substituted aryl magnesium halides and halides of monocarboxylic acids form ketones as the sole product of their reaction, no matter what the reaction conditions are.

3. Monoortho-substituted aryl magnesium halides and primary alkylmagnesium halides with sufficiently long chains, as well as secondary and tertiary alkylmagnesium halides, form ketones only under certain conditions (equimolecular proportions of the reacting substances, reverse order of mixing, etc.).

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CONDENSATION OF BENZYL ALCOHOL WITH DIATOMIC PHENOLS

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In a report by one of the present authors and I. Kurlina it was shown that phenol and some of its derivatives condense with benzyl alcohol in the presence of catalysts - sulfuric acid, sulfanilic acid, or activated clay (Chasov-Yar). Of the two possible reactions that occur - condensation of molecules of benzyl alcohol with one another or with the phenol - the latter predominates. This results in a mixture of ethers and benzylated phenols. We were interested in learning whether this reaction also holds good for diatomic phenols. With this in mind, we carried out a series of experiments on the condensation of benzyl alcohol with resorcinol and pyrocatechol. As catalyst we used Georgian clays: gumbrin (a clay from the village of Gumbri) and askanite (a clay activated with sulfuric acid). The reaction was faster when the latter clay was employed, but involved considerable tarring in all cases. We were able to isolate dihydroxyphenolmethanes from the condensation products: 2,4-dihydroxydiphenylmethane from resorcinol and the hitherto unknown 3,4-dihydroxydiphenylmethane from pyrocatechol (crystals with a m.p. of 92-94°). Their structure was demonstrated by fusion with caustic potash and copper oxide, the former yielding benzoic and 2,4-dihydroxybenzoic acids, and the second yielding benzoic and protocatechuic acids. Thus, under the conditions of our experiments benzyl alcohol condenses with diatomic phenols, liberating water and with the benzyl group entering the para position toward one of the dihydroxybenzene's hydroxyl groups.

EXPERIMENTAL

The experiments were performed in a flask equipped with a water trap and a reflux condenser. Toluene or benzene was used as the solvent; when the latter was used, the condensate was yellow, whereas toluene gave the product a dark-brown color. In all our experiments we used 0.1 mole of dihydroxybenzene and of benzyl alcohol, 3 g of the catalyst, and 57 ml of the solvent. Gumbrin proved to be less suitable, as it slowed down the reaction, which took 7 hours, whereas it took only 1 hour when askanite was used. The course of the reaction could easily be followed by checking the amount of water collected in the trap.

The askanite was desiccated at 100-110° and then kept in an exsiccator. In the experiment using resorcinol in a benzene solution and a mixture temperature of 83-86°, 1.9 ml of water was evolved in 1 hour instead of the 1.8 ml required by theory. The benzene was driven off, the residue washed several times with water to remove most of the unreacted resorcinol. The condensate was then dissolved in ether, desiccated with sodium sulfate, and - after the ether had

* Deceased

been driven off - distilled in vacuum (6 mm). Distillation of 18 g of the substance yielded 3 fractions: 1) b.p. 103-105°; 2) 130-190°, 1 g; and 3) 191-194° at 4 mm, 4 g. 10 g of a black tarry mass was left in the distilling flask. The first fraction proved to be resorcinol (m.p. 116-118°, no depression when mixed with resorcinol). The second fraction was not investigated; the third was a thick, transparent liquid that crystallized completely when kept in the exsiccator. M.p. 76-78°, corresponding to the figure in the literature for 2,4-dihydroxydiphenylmethane [1]. Analysis of this substance confirmed this formula.

0.1126 g substance: 0.3222 g CO₂; 0.0584 g H₂O.
0.0348 g substance: 0.5212 g camphor: Δt 13°.

Found %: C 78.05; H 5.80; M 205.5.

C₁₃H₁₂O₂ Calculated %: C 77.96; H 6.05; M 200.1.

0.1064 g substance: 28.4 ml CH₄ (22°, 729 mm).

C₁₃H₁₀(OH)₂. Calculated : 27.8 ml CH₄.

8 g of dihydroxydiphenylmethane, 6 g of copper oxide, and 24 g of potassium hydroxide in powdered form were heated in a nickel crucible for two hours at 210-250° with constant stirring. The melt was treated with water, and the solution filtered, acidulated with hydrochloric acid, and extracted with ether. After the ether had been driven off, the residue was dissolved in hot water. Upon cooling, crystals of benzoic acid (m.p. 121°, no depression when mixed with benzoic acid) settled out. The mother liquor was evaporated to dryness, and the residue carefully heated over a sand bath to 140° to drive off traces of benzoic acid. The new residue was dissolved in a small quantity of hot water. Upon cooling, white acicular crystals settled out, which were reduced with Fehling solution when heated. In titration, 0.0159 g required 10.2 ml of 0.01N sodium hydroxide; 10.3 ml are required for dihydroxybenzoic acid.

Thus, condensation of resorcinol with benzyl alcohol in the presence of askanite yielded 2,4-dihydroxyphenylmethane with a yield of 20% of the theoretical. It is quite likely that a certain amount of 2,6-dihydroxydiphenylmethane was synthesized in this reaction, in addition to the above isomer. This is indicated by the fact that the dihydroxybenzoic acid synthesized by oxidation colored a dilute solution of ferric chloride violet, whereas a concentrated solution was colored blue, which is characteristic of 2,6-dihydroxybenzoic acid.

The same quantities of reagents were used for the experiment with pyrocatechol. The reaction took 3 hours, 1.6 ml of water being evolved (instead of the 1.8 ml required by theory). After the same sort of treatment as that described above, the following fractions were obtained when the product was distilled at 5 mm pressure: 1) up to 105°, 0.8 g; 2) 171-178°, 1 g; and 3) 179-181°, 3.5 g. 10 g of a black oily mass remained in the distilling flask. When the third fraction was left in the exsiccator, it solidified into crystals with a m.p. of 92-94°. Analysis of these crystals yielded the following results.

0.1612 g substance: 0.4594 g CO₂; 0.0948 g H₂O.
0.0162 g substance: 0.2296 g camphor: Δt 14°.

Found %: C 77.73; H 6.58; M 201.6.

C₁₃H₁₂O₂. Calculated %: C 77.96; H 6.05; M 200.1.

0.0418 g substance: 10.6 ml CH₄ (19°, 723 mm).

C₁₃H₁₀(OH)₂. Calculated: 10.8 ml CH₄.

8 g of the substance, 6 g of copper oxide, and 24 g of potassium hydroxide were heated in a copper crucible for 4 hours at 240-275°. The melt was dissolved in water, and the solution filtered, acidulated with hydrochloric acid, and extracted with ether. After the ether had been driven off, the residue was dissolved in a small amount of hot water. Upon cooling, crystals of benzoic acid (m.p. 121°, mixed test sample with benzoic acid) separated out. The mother liquor was evaporated, and the residue heated to 140° to drive off the benzoic acid and then dissolved in a few milliliters of hot water. Upon cooling, white crystals separated out; they fused with decomposition at 193-195° and turned a solution of ferric chloride blue green, turning red when ammonia was added. All these properties are characteristic of protocatechuic acid.

Thus, the product synthesized by condensing pyrocatechol with benzyl alcohol was shown to have the structure of 3,4-dihydroxydiphenylmethane. Condensation yield: 17.5% of the theoretical.

SUMMARY

It has been shown that resorcinol and pyrocatechol can be condensed with benzyl alcohol in the presence of activated clay (askanite) to form dihydroxydiphenylmethanes, the benzyl group entering the para position to the hydroxy group in the benzene ring. 3,4-Dihydroxydiphenylmethane was synthesized for the first time.

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CONTACT CONVERSION OF FURANIDINE, PYRROLIDINE AND THIOPHANE. XXII

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The reciprocal transformations of furan, pyrrole, and thiophene effected by one of the present authors [1] demonstrated that the conversion of heterocyclic compounds containing oxygen into ring compounds with other hetero atoms proceeds with the greatest ease. The inverse transition from nitrogen-containing or sulfur-containing heterocyclic compounds to heterocyclic compounds containing oxygen likewise takes place, but it is negligible in extent; the reciprocal conversion of pyrrole and thiophene into each other takes place with minor yields.

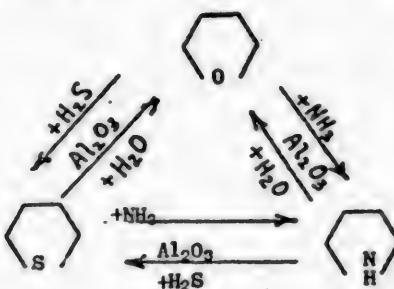
Inasmuch as the conversion of furanidine and pyrrolidine (by the action of ammonia upon the former in the presence of alumina at high temperature) proceeds with a yield of 46.5% [2], it was to be expected that the inverse transition from pyrrolidine to furanidine would take place with a small yield of furanidine. An even lower yield of furanidine was expected in the experiment on the conversion of thiophane to furanidine, since the reverse reaction — the conversion of furanidine into thiophane (by the action of hydrogen sulfide upon furanidine in the presence of alumina at high temperature) — takes place with an almost quantitative yield [2]. As for the reciprocal transformations of pyrrolidine and thiophane, the conversion of the former into the latter ought to be easier than the reverse reaction. Table 1 shows that the hypotheses set forth above were fully confirmed by the experimental data obtained in the present research.

TABLE 1

Transformation	Yield of reaction product (in % of theoretical, based on:	
	Substance introduced into the reaction	Substance employed in the reaction
Furanidine → pyrrolidine [2]...	46.5	-
Furanidine → thiophane [2]....	90.5	-
Pyrrolidine → furanidine.....	2.8	4.0
Thiophane → furanidine.....	0.9	4.5
Pyrrolidine → thiophane.....	10.5	35.5
Thiophane → pyrrolidine.....	1.0	4.0.

Thus, it has been shown for the first time in the present paper that the

complete hydrides of the simplest five-membered heterocyclic compounds - furanidine, pyrrolidine, and thiophane - may likewise undergo contact transformation.



EXPERIMENTAL

Conversion of Pyrrolidine into Thiophane

6.6 g of pyrrolidine, b.p. 85.4-86.4° (748 mm), d_4^{20} 0.8576, n_D^{20} 1.4428, was passed at a rate of 9-10 drops per minute in a stream of hydrogen sulfide through a tube filled with alumina and heated to 400°. The catalyzate was extracted with ether; the ether extract was treated with 2N hydrochloric acid, washed with water, and desiccated with calcium chloride. After the ether had been driven off, 0.7 g of thiophane was distilled over at 118-119°; it possessed the following constants after redistillation over sodium:

B.p. 118-119° (744 mm); d_4^{20} 0.9971; n_D^{20} 1.5045; MR_D 26.28.

C_4H_8S . Calculated: MR_D 26.44.

M.p. of compound with $HgCl_2$: 124.5-125°.

Found %: S 36.28, 36.31.

C_4H_8S . Calculated %: S 36.38.

Literature data for thiophane: Y.K.Yuryev and V.A.Tronova [2]: B.p. 119.8-120° (760 mm); d_4^{20} 0.9960; n_D^{20} 1.5052.

After the hydrochloride solution had been evaporated to dryness, and the dry residue treated with a 50% solution of potassium hydroxide, distillation from a flask fitted with a tall dephlegmator yielded 4.5 g of unchanged pyrrolidine. Yield of thiophane: 10.5% of the theoretical, in terms of the amount introduced into the reaction, and 35.5% in terms of the pyrrolidine used up in the reaction.

Conversion of Thiophane into Pyrrolidine

23.5 g of thiophane, b.p. 119.8-120° (760 mm), d_4^{20} 0.9960, n_D^{20} 1.5052, was passed at a rate of 9-10 drops per minute in a stream of ammonia through a tube filled with alumina and heated to 400°. The catalyzate was desiccated with potassium hydroxide and distilled with a tall dephlegmator, the 70-90° fraction being taken. This fraction was again desiccated with potassium hydroxide and, after it had been driven off from the caustic potash, again distilled over granules of sodium. Yield: 0.25 g of pyrrolidine, possessing the following constants:

B.p. 85-86° (750 mm); n_D^{20} 1.4460; m.p. of the picrate (after recrystallization from alcohol) 111-112°.

Found %: N 19.63, 19.67.
 C_4H_8N . Calculated %: N 19.71.

Literature data for pyrrolidine: Y.K.Yuryev and V.A.Tronova [2]: B.p. 85.4-86.4° (748 mm); d_4^{20} 0.8576; n_D^{20} 1.4428; picrate b.p. 112°.

The residue of the first distillation was extracted with ether; after the ether had been driven off from the ether solution, which had previously been desiccated with calcium chloride, 17.5 g of unreacted thiophane was distilled over at 117-119°. The yield of pyrrolidine was 1.0% of the theoretical, in terms of the thiophane placed in the reaction, and 4.0% in terms of the thiophane that was used in the reaction.

Conversion of Thiophane into Furanidine

25 g of thiophane and water (1:4 molecular ratio) were passed over alumina together at 400°. Distillation of the catalyzate (with a tall diphlegmator) yielded 0.3 g of a 60-67° fraction with n_D^{20} 1.4417, which possessed the characteristic strong odor of furanidine, mixed with the odor of thiophane, however. The presence of thiophane is also indicated by the high refractive index of this fraction (n_D^{20} 1.4091 for pure furanidine). Mixtures of furanidine and thiophane were prepared and their refractive indexes measured (Table 2) in order to determine the percentage of furanidine in this fraction.

TABLE 2

Refractive Indexes of Mixtures of Thiophane and Furanidine

Mixture No.	Quantity, g		Quantity of furanidine (% by wt.)	n_D^{20} of mixture
	Thiophane	Furanidine		
1	0.3262	0.1958	37.5	1.4660
2	0.3204	0.2978	48.0	1.4552
3	0.2878	0.4290	59.9	1.4448
4	0.2900	0.6806	70.1	1.4312

It is seen in Table 2 that the fraction with a b.p. of 60-67° and a n_D^{20} 1.4417 ought to have more than 60% (by weight) of furanidine. 20 g of unchanged thiophane was recovered from the residue by distillation.

Thus, when thiophane is converted into furanidine, the yield of the latter was 0.9% of the theoretical in terms of the thiophane placed in reaction and 4.5% in terms of the thiophane used up in the reaction.

Conversion of Pyrrolidine into Furanidine

10.5 g of pyrrolidine mixed with water (molecular ratio = 1:4) was passed over alumina at 400°. Hydrochloric acid (sp. gr. 1.16) was added in slight excess to the catalyzate, after which the mixture was distilled from a

* There is an unfortunate typographical error in the data on the constants of pyrrolidine in the monograph "Conversion of heterocyclic compounds containing oxygen into ring compounds with other hetero atoms and into hydrocarbons". (Sci. Rep. Moscow State Univ. 79, 1945), on p. 145, 7th line from the bottom: d_4^{20} 0.9576 should read d_4^{20} 0.8576.

flask equipped with a high dephlegmator. The 60-70° fraction collected during this first distillation was redistilled (after desiccation) over sodium. 0.3 g of furanidine was recovered, possessing the following constants:

B.p. 65° (750 mm); n_D^{20} 1.4085.

Literature data for furanidine: Y.K.Yuryev and M.D.Prokina [2]: b.p. 65-65.5° (750 mm); d_4^{20} 0.8899; n_D^{20} 1.4091.

3 g of unreacted pyrrolidine was recovered from the pyrrolidine hydrochloride. The yield of furanidine was 2.8% of the theoretical in terms of the pyrrolidine placed in the reaction and 4% in terms of that used in the reaction.

SUMMARY

In the present paper it has been shown for the first time that complete hydrides of the simplest five-membered heterocyclic compounds - furanidine (tetrahydrofuran), pyrrolidine, and thiophane (like furan, pyrrole, and thiophene) undergo contact conversion at high temperature, being reciprocally transformed into one another.

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CONVERSION OF α - AND β -ALKYL FURANIDINES INTO THE
CORRESPONDING THIOPHANES. XXIII

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In previous reports one of the present authors demonstrated that furanidine (tetrahydrofuran), as well as its α -alkyl homologues - α -methyl- and α, α' -dimethylfuranidine - are converted into the corresponding thiophanes when acted upon by hydrosulfide at high temperature in the presence of alumina [1].

In the present paper we have investigated the behavior of the α - and β -alkyl homologues of furanidine in such a conversion:



where R = CH₃, C₂H₅, C₃H₇, C₄H₉;

Constants of α - and β -Alkylthiophanes

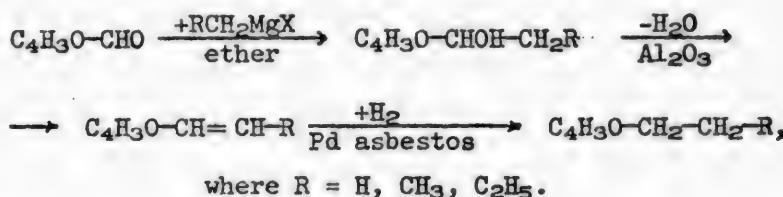
Thiophane homologue	Reaction temp.	Yield (in % of the theoretical)	Constants of the thiophane homologues		M_{D}	
			Boiling point	d_4^{20}	n_D^{20}	Found
α -Methylthiophane	350°	65.0	131.2-131.9° (747 mm)	0.9583	1.4927	30.96
	400	52.0				
β -Methylthiophane	350°	81.0	136.9-137.3° (747 mm)	0.9630	1.4932	30.81
	350	75.0				
α -Ethylthiophane	300	64.0	156.8-157.4° (745 mm)	0.9433	1.4900	35.63
	350	75.0				
β -Ethylthiophane	350	63.0	164.5-165.4 (750 mm)	0.9497	1.4911	35.43
	350	72.0				
α -Propylthiophane	350	63.0	179.3-179.8° (743 mm)	0.9308	1.4862	40.07
	350	72.0				
β -Propylthiophane	350	72.0	187.1-187.6° (733 mm)	0.9375	1.4886	40.07
	350	72.0				
α -Butylthiophane	300	68.0	201.5-202° (753 mm)	0.9221	1.4862	44.90
	350	60.0				
β -Butylthiophane	300	78.0	209.5-209.9° (733 mm)	0.9271	1.4868	44.76
	350	79.0				
β -Butylthiophane	400	56.0				

we found that in all the cases we investigated, the β -alkylthiophanes were synthesized with better yields than the α -alkylthiophanes, which must, it seems, be attributed to the high stability of the beta alkyl homologues of furanidine as well as of the beta alkyl homologues of thiophane. It was also found that as the number of carbon atoms in the side chain of the α - and β -alkylfuranidines rises, the optimum conversion temperature drops appreciably. The constants of the β -alkylthiophanes (boiling point, density, and refractive index) are higher than the constants of the α -alkylthiophanes, as was the case with the alkyl homologues of furanidine. This may be seen from the data in the table.

EXPERIMENTAL

I

The α -ethyl-, α -propyl-, and α -butylfuranidines* were synthesized from furfural and alkylmagnesium halides, as follows:



Synthesis of alkylfurylcarbinols. The use of an excess of RCH₂MgX in the reaction and deep chilling made it possible to obtain higher yields of the alkylfurylcarbinols than were achieved by F. Peters and R. Fischer, [2].

A solution of 1 mole of furfural in 150 ml of absolute ether was added during 2 hours, with vigorous stirring and chilling to -15° and -20°, to the alkylmagnesium halide, prepared from 1.5 mole of the alkyl halide (methyl iodide, ethyl bromide, or propyl bromide) dissolved in 250 ml of absolute ether (in a three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser with a calcium chloride tube). After the freezing mixture had been removed, the reaction mass was heated over a water bath for 30 minutes. Upon cooling, decomposition was effected by a quantity of water sufficient to produce a thick paste of the magnesium hydroxide. The ether solution was decanted, and the residue washed 4 to 5 times with ether (while stirred). The combined ether extracts were shaken up with a 40% solution of sodium bisulfite and desiccated with calcined potash after separation. The next day 10-12 drops of aniline was added (to remove the last traces of acid), the ether was driven off, and the alkylfurylcarbinols were distilled at reduced pressure.

Methyl- α -furylcarbinol. Yield: 79 g (70% of the theoretical); b.p. 76-77° (23 mm); d₄²⁰ 1.0790; n_D²⁰ 1.4808.

Literature data: b.p. 76-77° (23 mm); d₂₅²⁵ 1.0771; n_D²⁵ 1.4785 [2].

Ethyl- α -furylcarbinol. Yield: 111 g (89% of the theoretical); b.p. 74.5-75.5° (10 mm); d₄²⁰ 1.0432; n_D²⁰ 1.4761.

Literature data: b.p. 57-58° (6 mm); 89-90° (23 mm); d₂₀²⁰ 1.0474; n_D²⁰ 1.4759 [2].

* γ -Ethylfuranidine was synthesized by the catalytic hydrogenation of α -methylfuran. The synthesis of the β -alkylfuranidines was described in our previous report (Jour. Gen. Chem. USSR, 18, 1811 (1948)).

Propyl- α -furylcarbinol. Yield 87 g (62% of the theoretical); b.p. 85-86° (10 mm); d_4^{20} 1.0197; n_D^{20} 1.4789.

Literature data: b.p. 76-77° (5 mm) 84-85° (9 mm); 91-92° (12 mm); d_{25}^{25} 1.0179; n_D^{25} 1.4768 [2].

Synthesis of furylalkenes. Alkyl- α -furylcarbinols were dehydrated over alumina at 400° in a weak current of nitrogen. The catalysis product was impregnated with potash, separated from its water, dessicated, and distilled in a current of nitrogen. Distillation yielded fractions boiling over wide ranges and containing furylalkenes as well as furylalkanes. According to R. Paul [3], the latter are formed alongside the furylalkenes whenever alkylfurylcarbinols are dehydrated. 79 g of methyl- α -furylcarbinol yielded 30 g of a fraction with a boiling point of 86-97°. 111 g of ethyl- α -furylcarbinol yielded 40 g of a 115-132° fraction. 87 g of propyl- α -furylcarbinol yielded 36 g of a 72-95° (93 mm) fraction.

Synthesis of α -alkylfuranidines. α -Alkylfuranidines were synthesized by the catalytic hydrogenation of mixtures of furylalkenes and furylalkanes over palladinized asbestos. The catalytic hydrogenation of compounds of the furanidine series with unsaturated side chains was accomplished for the first time in our research. Hydrogenation was effected at 150° at the rate of 6-7 drops per minute (160° for α -butylyfuranidine by the hydrogenation of a mixture of equal volumes of the furylalkene and furan). Bromine [4] was added to the catalyzate (to eliminate the last traces of furan compounds) until the solution turned yellow; the next day - after distillation to remove the bromides - the preparations were fractionated twice over sodium from a flask fitted with a dephlegmator.

α -Ethylfuranidine: b.p. 105-106.5° (746 mm); d_4^{20} 0.8595; n_D^{20} 1.4170; MR_D 29.29; $C_6H_{12}O$. Calculated MR_D 29.23.

Literature data: H. Burdick and H. Adkins [5]; b.p. 105-107° (740 mm); d_4^{25} 0.849; n_D^{25} 1.4145; N.I. Shuikin and Assoc. [6] b.p. 107.5-109° (751 mm); d_4^{20} 0.8563; n_D^{20} 1.4165; R. Paul [4]: b.p. 108° (758 mm); d_{15}^{11} 0.866; n_D^{11} 1.41905; Y.K. Yuryev and assoc. [7]: b.p. 106.8-107.5° (743 mm); d_4^{20} 0.8551; n_D^{20} 1.4161.

α -Propylfuranidine: b.p. 132-133° (738 mm); d_4^{20} 0.8547; n_D^{20} 1.4237; MR_D 34.02; $C_7H_{14}O$. Calculated MR_D 33.85.

Literature Data: H. Burdick and H. Adkins [5]: b.p. 132-133° (739 mm); d_4^{25} 0.8533; n_D^{25} 1.4230; N.I. Shuikin and assoc. [8]: b.p. 132-133° (756 mm); d_4^{20} 0.8548; n_D^{20} 1.4242; R. Paul [4]: b.p. 135° (773 mm); d_{15}^{10} 0.863; n_D^{10} 1.4255.

α -Butylyfuranidine: b.p. 158-159° (750 mm); d_4^{20} 0.8554; n_D^{20} 1.4287; MR_D 38.59. $C_8H_{16}O$. Calculated MR_D 38.47.

Literature data: R. Paul [4]: b.p. 159-160° (768 mm); d_{15}^9 0.8626; n_D^9 1.43145.

II

The alkylfuranidines were passed through a tube filled with alumina at high temperature at a rate of 10-12 drops per minute in a current of hydrogen

sulfide. The receiving vessel was chilled with a mixture of snow and salt. The ether extracts of the catalyzates were washed with a solution of potassium hydroxide and dessicated by fusion with caustic potash. After the ether had been driven off, the reaction product was carefully fractionated from a flask equipped with a dephlegmator.

Conversion of α -Alkylfuranidines Into α -Alkylthiophanes

α -Methylthiophane: 8.7 g of α -methylthiophane, with a b.p. of 131-133° (65% of the theoretical yield), was synthesized from 11.2 g of α -methylfuranidine at 350°. 2.9 g of α -methyl-thiophane, with a b.p. of 131-133° (54% of the theoretical yield), was synthesized from 5.8 g of α -methylfuranidine at 400°.

After redistillation the α -methylthiophane exhibited the following constants:

B.p. 131.2-131.9° (747 mm); d_4^{20} 0.9583; n_D^{20} 1.4927; MR_D 30.96.
 $C_5H_{10}S$. Calculated MR_D 31.06.

Literature data: E. Grishkevich-Trokhimovsky [9]: b.p. 132.5-132.6° (750 mm); d_4^{18} 0.9564; n_D^{18} 1.4886; Y.K. Yuryev [1]: b.p. 131.2-131.5° (756 mm); d_4^{20} 0.9541; n_D^{20} 1.4922.

α -Ethylthiophane: 5.5 g of α -ethylthiophane (62% of the theoretical yield) with a b.p. of 156-157° at 743 mm was synthesized from 7.7 g of α -ethylfuranidine at 300°. At 350°, 6.4 g of α -ethylthiophane (71% of the theoretical yield) was synthesized from 7.8 g of α -ethylfuranidine.

After redistillation, α -ethylthiophane had the following constants:

B.p. 156.8-157.4° (745 mm); d_4^{20} 0.9433; n_D^{20} 1.4900; MR_D 35.63.
 $C_6H_{12}S$. Calculated: MR_D 35.67.

Literature data: Y.K. Yuryev [1]: b.p. 155.5-156.5° (753 mm); d_4^{20} 0.9451; n_D^{20} 1.4896.

α -Propylthiophane: 5.1 g of α -propylthiophane (63% of the theoretical yield) was synthesized from 7.2 g of propylfuranidine at 350°.

B.p. 179.3-179.8° (743 mm); d_4^{20} 0.9308; n_D^{20} 1.4862; MR_D 40.07.
 $C_7H_{14}S$. Calculated: MR_D 40.30.

M.p. of the compound with $HgCl_2$: 51-52°.

3.107 mg substance: 5.523 mg $BaSO_4$.
4.622 mg substance: 8.267 mg $BaSO_4$.

Found %: S 24.41, 24.56.
 $C_7H_{14}S$. Calculated %: S 24.62.

α -Propylthiophane is not described in the literature.

α -Butylthiophane: 3.8 g of α -butylthiophane (68% of the theoretical yield), distilled at 201-202°, was synthesized from 5 g of α -butylfuranidine at 300°. At 350° 3.4 g of α -butylthiophane (60% of the theoretical yield) was synthesized from 5.1 g of α -butylfuranidine.

After redistillation, α -butylthiophane had the following constants:

b.p. 201.5-202° (753 mm); d_4^{20} 0.9221; n_D^{20} 1.4862; MR_D 44.90.

$C_8H_{16}S$ Calculated: MR_D 44.91.

M.p. of compound with $HgCl_2$: 39.5-41°.

4.229 mg substance: 6.815 mg $BaSO_4$.

5.396 mg substance: 8.705 mg $BaSO_4$.

Found %: S 22.13, 22.15.

$C_8H_{16}S$. Calculated %: S 22.22.

α -Butylthiophane is not described in the literature.

Conversion of β -Alkylfuranidines into β -Alkylthiophanes

β -Methylthiophane. 9.4 g of β -methylthiophane (81% of the theoretical yield) was synthesized at 350° from 9.8 g of β -methylfuranidine.

B.p. 136.9-137.8° (747 mm); d_4^{20} 0.9630; n_D^{20} 1.4932; MR_D 30.81.

$C_5H_{10}S$. Calculated: MR_D 31.06.

M.p. of compound with $HgCl_2$: 107.5 - 108.5°.

3.378 mg substance: 7.696 mg $BaSO_4$.

4.841 mg substance: 11.008 mg $BaSO_4$.

Found %: S 31.29, 31.23.

$C_5H_{10}S$. Calculated %: S 31.37.

Literature data: E. Grishkevich-Trokhimovsky [10]: b.p. 137.5-138.5° (740 mm); $d_4^{18.5}$ 0.9596; $n_D^{18.5}$ 1.4886; M.p. compound with $HgCl_2$: 82-83°.

β -Ethylthiophane. 5.1 g of β -Ethylthiophane (80% of the theoretical yield) was synthesized at 350° from 5.5 g of β -ethylfuranidine.

B.P. 164.5-165.4° (750 mm); d_4^{20} 0.9497; n_D^{20} 1.4911; MR_D 35.43.

$C_6H_{12}S$. Calculated MR_D 35.67.

M.p. of compound with $HgCl_2$: 112-112.5°.

4.832 mg substance: 9.611 mg $BaSO_4$.

3.979 mg substance: 7.960 mg $BaSO_4$.

Found %: S 27.45, 27.47.

$C_6H_{12}S$. Calculated %: S 27.59.

β -Ethylthiophane is not described in the literature.

β -Propylthiophane. 5.3 g of β -propylthiophane (72% of the theoretical yield) was synthesized at 350° from 6.8 g of β -propylfuranidine.

B.p. 187.1-187.6° (733 mm); d_4^{20} 0.9375; n_D^{20} 1.4886; MR_D 40.07.

$C_7H_{14}S$. Calculated: MR_D 40.30.

M.p. of compound with $HgCl_2$: 92-92.5°.

3.731 mg substance: 6.651 mg $BaSO_4$.

5.270 mg substance: 9.415 mg $BaSO_4$.

Found %: S 24.48, 24.53.

$C_7H_{14}S$. Calculated %: S 24.62.

β -Propylthiophane is not described in the literature.

β -Butylthiophane: 4.1 g of β -butylthiophane (78% of the theoretical yield), which distilled at 209-210°, was synthesized at 300° from 4.7 g of β -butylfuranidine. At 350°, 4.5 g of β -butylthiophane (79% of the theoretical yield) was synthesized from 5.1 g of β -butylfuranidine. At 400°, 2.9 g of β -butylthiophane (56% of the theoretical yield) was synthesized from 4.5 g of β -butylfuranidine.

After redistillation, β -butylthiophane had the following constants:

B.p. 209.5-209.9° (733 mm); d_4^{20} 0.9271; n_D^{20} 1.4868; M_R 44.76.

$C_8H_{16}S$. Calculated: M_R 44.91.

M.p. of compound with $HgCl_2$: 96-96.5°.

5.542 mg substance: 8.923 mg $BaSO_4$.

Found %: S 22.11, 22.03.

$C_8H_{16}S$. Calculated %: S 22.22.

β -Butylthiophane is not described in the literature.

SUMMARY

1. In the present research α -alkyl- and β -alkylthiophanes (tetrahydrothiophenes), up to and including α -butyl- and β -butyl-thiophane, have been synthesized from α -alkyl- and β -alkylfuranidines (tetrahydrofurans) by means of the catalytic conversion of heterocyclic compounds containing oxygen into ring compounds with other hetero atoms.

2. β -Alkylthiophanes are synthesized with higher yields (72-81% of the theoretical yield) than α -alkylthiophanes (65-70% of the theoretical yield).

3. The optimum temperature for the conversion of the homologues of furanidine into homologues of thiophane is lower than the optimum temperature for the conversion of furanidine itself into thiophane.

4. The optimum yields of the homologues of thiophane are lower than the yields of thiophane itself, although the complexity of the alkyl group in the initial alkylfuranidines has no noticeable effect upon the yields of the thiophane homologues.

5. The β -alkylthiophanes have higher boiling points, densities, and refractive indexes than the α -alkylthiophanes.

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REACTION OF DIETHYL MERCURY WITH PHENOLS. V.

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It has been previously shown [1] that diphenylmercury, as well as other aromatic derivatives of mercury (dinaphthylmercury and ditolyl mercury) that contain organic radicals standing at the head of the Nesmeyanov-Karash series of comparative reactivities, are able to mercurize the phenols. This results in mono-, di-, and trimercurized derivatives of the phenols, with the Hg-aryl radicals entering the benzene ring. Subsequently, with dibenzylmercury as an example, it was shown [2] that compounds of mercury with radicals that are situated at the end of the Nesmeyanov-Karash series (such as benzyl) do not form stable mercuration compounds when reacted with the phenols, the reaction continuing until metallic mercury is liberated. It was of some interest to investigate the reaction with the phenols of the mercury derivatives in which the organic radicals linked to the mercury were at neither end of the comparative-reactivity series of radicals, but were located at the center of the series. Diethylmercury was selected as a compound of this kind. There is no indication in the literature concerning the feasibility of this sort of reaction.

The reaction of diethylmercury with the following phenols was investigated: 1) phenol; 2) p-bromophenol; 3) 2,4,6-tribromophenol; 4) 2,4-dichlorophenol; 5) 2,4,6-trichlorophenol; 6) bromohydroquinone; 7) p-nitrophenol; 8) o-nitrophenol; 9) resorcinol; and 10) pyrogallol. The reaction was effected at 100-130° without a solvent, as well as in a solution of ethyl alcohol.

Diethylmercury differs from the aromatic compounds of mercury in that it forms monomercurated derivatives with the phenols in the form of crystalline substances that are easily soluble in organic solvents and alkaline solutions.

The reaction of diethylmercury with the phenols may be represented by the following equation:



Only when diethylmercury is reacted with resorcinol or pyrogallol are dimercurated derivatives formed; these are infusible and only slightly soluble.

The velocity of reaction of diethylmercury with the phenols is governed by the nature, quantity, and mutual arrangement of the substituent groups in the phenol's benzene ring. Regularities of the same order as those discovered in the reaction of diphenylmercury with various phenols [1] have been found to exist.

It was shown that the rate of reaction of the phenols with diethylmercury

is sharply increased as the number of hydroxyl groups in the phenol molecule rises: pyrogallol liberates 100% of metallic mercury, resorcinol liberates 38.6% of metallic mercury and forms a dimercurated derivative, and phenol liberates 1.8% of metallic mercury while forming a monomercurated derivative.

The difference in the behavior of para and ortho nitrophenols in the reaction with diethylmercury is of interest: p-nitrophenol precipitates 18.6% of metallic mercury and forms a monomercurated derivative, whereas o-nitrophenol precipitates 5% of metallic mercury without forming any mercuration products. When no solvent is present, tribromophenol, trichlorophenol, dichlorophenol, and bromophenol form monomercurated derivatives with diethylmercury, precipitating a small amount of metallic mercury (2-4%), but if the reaction is carried out in a solution of ethyl alcohol, the quantity of metallic mercury that is precipitated rises sharply (as high as 19%), while the quantity of monomercurated derivatives decreases.

The behavior of bromohydroquinone is particularly interesting. This compound, which contains two hydroxyl groups in addition to the bromine atom, enters into reaction with diethylmercury readily, forming at 100° a mixture of mono- and dimercurated derivatives, and at 130° only a dimercurated compound with no precipitation of metallic mercury, which indicates the stability of the reaction products.

EXPERIMENTAL

The diethylmercury was prepared by the Gilman and Braun method [3]: reacting mercuric bromide with an ether solution of ethylmagnesium bromide. The diethylmercury thus synthesized had a b.p. of 158-160° and a specific gravity of 2.426. All our experiments on the reaction of diethylmercury with the phenols were performed by heating a mixture of the substances in sealed glass ampoules immersed in an oil thermostat. In all our experiments 0.3 g of the phenol was used for 0.3 g of diethylmercury. After heating, most of the ampoules opened with a blast, releasing a combustible gas (ethane).

1. Diethylmercury and phenol. Experiment 1. (100°, 3 hours). After the heating a small amount of metallic mercury (1.04%) separated out without any new compounds being formed.

Experiment 2 (130°, 3 hours). Metallic mercury (0.0042 g - 1.80%) separated out. The contents of the ampoule were treated with anhydrous ether, causing white acicular crystals to settle out. They were purified by recrystallization from alcohol and ether.

Yield: 0.12 g, m.p. 113-114°.

0.0542 g substance: 3.38 ml 0.1N NH₄CNS.

Found %: Hg 62.36.

C₂H₅HgC₆H₄OH. Calculated %: Hg 62.18.

The synthesized substance is easily soluble in alkaline solutions. Treatment with an alcoholic solution of HCl causes ethylmercury chloride, with a m.p. of 189-190° (mixed test sample 190°), to form. Thus, the reaction of diethylmercury upon phenol produces a monomercurated derivative of phenol.

2. Diethylmercury and resorcinol. Experiment 1. (100°, 3 hours). After

the heating, metallic mercury was observed to separate out (0.0034 g - 1.46%), and a pink crystalline mass formed, which was insoluble in organic solvents, but dissolved in alkalis. Yield: 1 g of a substance, infusible up to 180° (decomposes above that point).

0.0604 g substance: 4.25 ml 0.1N NH₄CNS.
Found %: Hg 70.36.
(C₂H₅Hg)₂C₆H₂(OH)₂. Calculated %: Hg 70.73.

Experiment 2 (130°, 3 hours). Metallic mercury (0.09 g - 38.62%) and 0.14 g of a pink insoluble substance with a m.p. of 180-181° with decomposition settled out.

0.0648 g substance: 4.57 ml 0.1N NH₄CNS.
Found %: Hg 70.52.
(C₂H₅Hg)₂C₆H₂(OH)₂. Calculated %: Hg 70.73

Thus, the reaction of diethylmercury with resorcinol at 100-130° results in the formation of a dimercurated derivative of resorcinol that is insoluble in organic solvents.

3. Diethylmercury and bromohydroquinone. Experiment 1 (100°, 3 hours). The color of the reaction mass was brown. After treatment with alcohol, the residue contained a white crystalline substance that is slightly soluble in benzene, m.p. 180-182° with decomposition. Yield: 0.12 g.

0.0632 g substance: 3.91 ml 0.1N NH₄CNS.
Found %: Hg 61.87.
(C₂H₅Hg)₂C₆HBr(OH)₂. Calculated %: Hg 62.09.

0.08 g of a crystalline substance with a m.p. of 163° was isolated from an alcohol solution.

0.0524 g substance: 2.50 ml 0.1N NH₄CNS.
Found %: Hg 47.71.
C₂H₅HgC₆H₂Br(OH)₂. Calculated %: Hg 48.03.

Experiment 2 (130°, 3 hours). The reaction takes place no matter whether alcohol is present or not. The main reaction product is insoluble in alcohol and slightly soluble in benzene. White crystals, m.p. 180° with decomposition. Yield: 0.3 g.

0.0596 g substance: 3.68 ml 0.1N NH₄CNS.
Found %: Hg 61.74.
(C₂H₅Hg)₂C₆HBr(OH)₂. Calculated %: Hg 62.09.

Thus, depending on the prevailing conditions of the reaction between diethylmercury and bromophenol, mono- and dimercurated bromophenol derivatives are formed at 100° and the dimercurated derivative at 130°.

4. Diethylmercury and pyrogallol. When diethylmercury is heated with pyrogallol at 100 and 130°, without a solvent and in an alcohol solution, metallic mercury is seen to separate out 100%, and considerable tarring occurs.

5. Diethylmercury and p-bromophenol. Experiment 1 (130°, 3 hours. No solvent). Metallic mercury (0.0071 g, 3.05%) is seen to settle out. Small

white crystals, with a m.p. of 92-94°, separated out of an alcohol solution. Yield: 0.08 g.

0.0554 g substance: 2.76 ml 0.1N NH₄CNS.

Found %: Hg 49.82.

C₂H₅HgC₆H₅(OH)Br. Calculated %: Hg 49.96.

Experiment 2. (130°, 3 hours, 3 ml alcohol). 0.0341 g (14.63%) of metallic mercury is seen to separate out and a monomercurated derivative is formed.

6. Diethylmercury and 2,4,6-tribromophenol. Experiment 1 (130°, 3 hours, no solvent). Metallic mercury (0.0061 g - 2.61%) is observed to settle out. The white crystalline mass is treated successively with alcohol and benzene. 0.3 g of a white crystalline substance, with a m.p. of 96-97°, is isolated from the benzene.

0.0560 g substance: 1.98 ml 0.1N NH₄CNS.

Found %: Hg 35.36.

C₂H₅HgC₆H₅(OH)Br₃. Calculated %: Hg 35.84.

Experiment 2 (130°, 3 hours, 3 ml alcohol). Metallic mercury (0.0457 g - 19.61%) is observed to settle out, and a monomercurated derivative is formed. Hence, as is the case with p-bromophenol, diethylmercury forms only a mono-mercurated derivative with 2,4,6-tribromophenol.

7. Diethylmercury and 2,4-dichlorophenol. Experiment 1. (130°, 3 hours, no solvent). Metallic mercury (0.0095 g - 4%) separates out. The reaction mass is a thick oil, easily soluble in organic solvents, which gradually crystallizes upon standing. It is hard to remove its impurities. Yield: 0.15 g.

0.0556 g substance: 2.57 ml 0.1N NH₄CNS.

Found %: Hg 46.22.

C₂H₅HgC₆H₅(OH)Cl₂. Calculated %: Hg 51.23.

Experiment 2 (130°, 3 hours, 3 ml alcohol). Metallic mercury (0.0359 g - 15.40%) separated out. The reaction of diethylmercury with 2,4-dichlorophenol results in the formation of a monomercurated derivative; we were unable to isolate it in pure form.

8. Diethylmercury and 2,4,6-trichlorophenol. Experiment 1. (130°, 3 hours, no solvent). Metallic mercury (0.0082 g - 3.52%) separated out. The white reaction mass was treated with alcohol to remove the unreacted trichlorophenol. The residue was recrystallized from benzene. 0.2 g of a white crystalline substance with a m.p. of 108-110° was obtained.

0.0582 g substance: 2.72 ml 0.1N NH₄CNS.

Found %: Hg 46.74.

C₂H₅HgC₆H₅(OH)Cl₃. Calculated %: Hg 47.08.

The synthesized compound dissolves easily in alkalis. The action of an alcoholic solution of HCl precipitates a crystalline deposit of ethylmercury chloride, with a m.p. of 188-190°. Mixed test sample 190°.

Experiment 2 (130°, 3 hours, 3 ml alcohol). Metallic mercury (0.0424 g - 18.20%) and 0.1 g of a monomercurated derivative separated out. Thus, diethylmercury and 2,4,6-trichlorophenol yield a monomercurated derivative.

9. Diethylmercury and p-nitrophenol (130° , 3 hours). Metallic mercury (0.0434 g - 18.65%) separated out. The reaction mass was greenish-brown; much of it dissolved in alcohol, from which the unreacted p-nitrophenol separated out upon standing. The insoluble deposit was dissolved in benzene; after removal of the benzene there remained 0.1 g of a soft, greenish brown mass that was hard to purify.

0.0648 g substance: 3.25 ml 0.1N NH_4CNS .

Found %: Hg 50.15.

$\text{C}_2\text{H}_5\text{HgC}_6\text{H}_3(\text{OH})\text{NO}_2$. Calculated %: Hg 54.56.

Thus, the product of the reaction of diethylmercury with p-nitrophenol is a monomericcurated derivative that cannot be isolated in pure form.

10. Diethylmercury and o-nitrophenol (130° , 3 hours). Metallic mercury (0.0120 g - 5.15%) separated out. The unreacted diethylmercury and o-nitrophenol were found in the residue.

SUMMARY

1. It has been established, for the first time, that diethylmercury is able to mercurate phenols, forming new asymmetrical derivatives.

2. In the mercuration of phenols, mono- and dimercurated derivatives are formed.

3. The velocity of the reaction between the phenols and diethylmercury depends upon the nature, the mutual arrangement, and the number of substituent groups in the phenol's benzene ring.

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REACTION OF DIAMYL MERCURY WITH PHENOLS. VI

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In his previous report [1], the author pointed out that when diethylmercury reacts with the phenols, its principal reaction products are the monomercurated derivatives of the latter, whereas the aromatic compounds of mercury mercurize the phenols to form mono-, di-, and trimercurated derivatives [2]. We were interested in examining the behavior of diamylmercury in reactions with phenols, in view of the fact that the n-amyl radical is below the ethyl radical and closer to benzyl in the series of comparative reactivities. The diamylmercury was reacted with the same 10 phenols that were used in the diethylmercury tests [1], at 100-130°.

Diamylmercury differs from diethylmercury in that it forms, with most of the phenols, viscous oily products that cannot be purified, at the same time precipitating metallic mercury in quantities that rise as high as 22% in some cases. Only when diamylmercury was reacted with bromohydroquinone and 2,4,6-trichlorophenol were we able to isolate the monomercurated derivatives of these phenols in the pure state.

EXPERIMENTAL

Di-n-amylmercury was prepared for the first time; it is not described in the literature. It was prepared by letting mercuric bromide act upon an ether solution of n-amylmagnesium bromide.

Di-n-amylmercury is a colorless liquid with a characteristic fruity odor. B.p. 104-106° at 4 mm; d_4^{20} 1.655.

All our experiments were performed under the same conditions as those described for diethylmercury. The quantities used were: 0.3 g of diamylmercury and 0.3 g of the phenols.

1. Di-n-amylmercury and bromohydroquinone. (130°, 3 hours.) The reaction mass was treated with alcohol to remove the excess of unreacted bromohydroquinone. The residue was recrystallized from benzene. Yield: 0.08 g; m.p. 118-119°.

0.0466 g substance: 2.01 ml 0.1N NH_4CNS .

Found %: Hg 43.13.

$\text{C}_5\text{H}_{11}\text{HgC}_6\text{H}_2(\text{OH})_2\text{Br}$. Calculated %: Hg 43.64.

Thus, analysis of the synthesized compound indicates that it is a monomercurated derivative of bromohydroquinone.

2. Di-n-amylmercury and 2,4,6-trichlorophenol. (130°, 3 hours). The reaction mass is an oil that is soluble in alcohol and benzene. Repeated recrystallization from benzene yielded 0.12 g of a crystalline substance with a m.p. of 50-52°.

0.0526 g substance: 2.185 ml 0.1N NH₄CNS.

Found %: Hg 41.54.

C₅H₁₁HgC₆H(OH)Cl₃. Calculated %: Hg 42.85.

The amount of metallic mercury separating out was 0.0166 g - 9.44%. Thus, the principal product of the reaction of the di-n-amylmercury with 2,4,6-trichlorophenol is a monomercurated derivative.

When di-n-amylmercury is reacted with the following phenols: 1) phenol; 2) p-nitrophenol; 3) dichlorophenol; 4) pyrogallol; 5) bromophenol; 6) tribromophenol; 7) resorcinol; and 8) hydroquinone, 2.0 g (22.76%) of metallic mercury is observed to separate out, and a thick tarry oil that cannot be analyzed is formed.

SUMMARY

1. Di-n-amylmercury was synthesized for the first time.
2. The reactions of di-n-amylmercury with various phenols were investigated.
3. It was demonstrated for the first time that di-n-amylmercury forms monomercurated derivatives when reacted with 2,4,6-trichlorophenol and bromohydroquinone.

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* See CB translation pp. 703-707.

THE PHOTOCHEMICAL REACTION OF ORGANOMETALLIC COMPOUNDS OF MERCURY IN SOLUTIONS

I. THE REACTIONS OF DIPHENYLMERCURY

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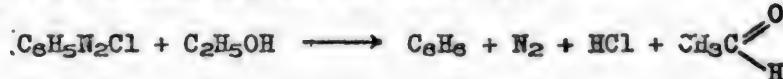
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When dimethylmercury or methylmercury chloride is photolyzed in the gaseous phase, methyl radicals are formed. Taylor and Jones [1] found these radicals in their polymerization of ethylene at temperatures in the 200-300° range. Terenin and Prilezhayeva [2] identified the radicals spectroscopically. Thompson and Linnet [3] characterized the methyl radical by its reaction with nitrous oxide.

We thought it would be of interest to investigate the reaction of organometallic compounds in solutions that, as far as we knew, had not been studied at all up to the present time. The object we chose for our research was diphenylmercury. In work published earlier [4] the formation of phenyl radicals during thermal reactions of diphenylmercury was demonstrated. One of these reactions was its action upon alcohols, in accordance with the following equation:

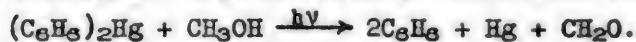


The phenyl radicals formed in the decomposition of diazo compounds react in exactly the same way with alcohols [5]:



The first substance employed in the photochemical reaction of diphenylmercury with alcohols was methanol, which reacts most easily with diphenylmercury upon heating, [6]

The photochemical reaction proceeded in accordance with a fully analogous equation, yielding mercury and forming benzene and formaldehyde:



The reaction was very smooth, only negligible quantities of diphenyl being liberated.

The next series of experiments was set up with solvents containing chlorine. As we know, diphenyl mercury has proved to be extremely inert when

heated with many halogen derivatives. Thus, Whitmore and Thurman [7] heated diphenyl- and ditolyl-mercury for 300-350 hours in a boiling solvent (carbon tetrachloride, toluene) without any reaction taking place with a large number of different halogen derivatives. Carbon tetrachloride was even proposed as an indifferent solvent. Koton, Zorina, and Osberg [8] also found that no reaction occurs between diphenylmercury and chloroform or bromoform when heated together to 130° in sealed tubes. It reacted only with iodoform, forming benzene, phenylmercury iodide, and C_2I_4 . It is evident that in the experiments described above dissociation of the phenyl-mercury bond has not been achieved, since phenyl radicals react readily with CCl_4 or $CHCl_3$. Thus, the phenyl radical yields chlorobenzene and the CCl_3 radical, which are further dimerized to hexachloroethane, in the decomposition of the following diazo compounds: $C_6H_5N_2Cl$ [9], $C_6H_5N_2OCOCH_3$ and $C_6H_5N_2OH$ [10]. The phenyl formed when tri-phenylmethaneazobenzene is heated in CCl_4 likewise yields chlorobenzene, the CCl_3^- and $(C_6H_5)C^-$ radicals joining together to form $(C_6H_5)_3CCl_3$. Chlorobenzene is also formed when benzoyl peroxide reacts with CCl_4 [11].

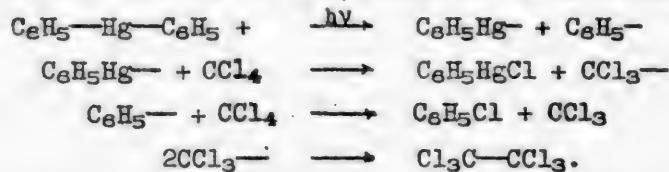
When heated with chloroform, however, benzoyl peroxide yields benzene. Hence, the phenyl radical reacts as follows:



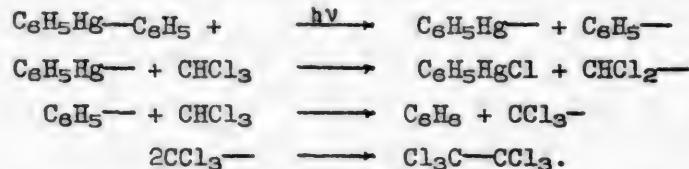
In both cases, the CCl_3 is converted into hexachloroethane. Hence, the same reactions might be expected to occur with diphenylmercury, if phenyl radicals are formed in its photolysis. And in fact, when solutions of diphenylmercury in CCl_4 , chloroform, dichloroethane, or tetrachloroethane, or its benzene solution with hexachloroethane are irradiated, the expected reaction takes place, phenylmercury chloride being formed in all instances.

When carbon tetrachloride is used as the solvent, chlorobenzene is formed, the other solvents, which contain hydrogen ($CHCl_3$, $C_2H_2Cl_4$, $C_2H_4Cl_2$), always yielding benzene.

The reaction with carbon tetrachloride is as follows:



The reactions with solvents containing hydrogen are:



What happens to the $-CHCl_2$ radical is still uncertain. It might be noted that in the second case ($CHCl_3$, $C_2H_2Cl_4$, $C_2H_4Cl_2$) the reaction involves the precipitation of an extremely small amount of metallic mercury. The hexachloroethane formed during these reactions may also take part in the reaction itself.

When a benzene solution of diphenylmercury and hexachloroethane is irradiated, phenylmercury iodide is evolved.

Research is continuing with other organic derivatives of mercury, and their photochemical reactions with other classes of compounds are being studied.

EXPERIMENTAL

The experiments were carried out in quartz test tubes. A PRK-2 mercury-quartz lamp served as the light source.

Diphenylmercury and methanol. 2.5 g of diphenylmercury in 25 ml of methanol was irradiated for 35 hours. After irradiation 1.2 g of mercury was isolated. The alcohol solution was distilled. The first fractions distilled yielded benzene (about 0.5 ml) when diluted with water; the benzene was nitrated to m-dinitrobenzene, with a m.p. of 90°. It caused no depression of the melting point when mixed with a sample of the pure product. The distillate had a strong odor of formaldehyde, and gave the aldehyde reaction. The distillation residue was distilled with steam. At first a negligible quantity of diphenyl was collected, with a m.p. of 69°; it caused no depression of the melting point when mixed with pure diphenyl. 0.3 g of unreacted diphenylmercury, with a m.p. of 125°, was found in the residue.

Diphenylmercury and carbon tetrachloride. 5 g of diphenylmercury in 75 ml of CCl_4 was irradiated in a quartz flask for 10 hours. Crystals of phenylmercury chloride settled out of the solution. Recrystallization from acetone yielded 3.0 g of the pure substance (68% of theory), with a m.p. of 257°; it caused no depression of the melting point when mixed with the pure product. The filtrate was steam distilled and nitrated. This yielded p-chloronitrobenzene, which had a m.p. of 83° after double recrystallization from alcohol, and caused no depression of the melting point when mixed with the pure substance. Together with carbontetrachloride we distilled a substance with a peculiar odor that was unaffected by strong acids and sublimed readily in a sealed capillary into crystals with a m.p. of 185°; it caused no depression of the melting point when mixed with pure hexachloroethane.

The residue remaining after steam distillation was a thick brown mass, from which another 0.6 g (13%) of phenylmercury chloride, with a m.p. of 257° after double recrystallization, was recovered by treatment with hot acetone. Thus, a total of 81% of the substance was synthesized, in terms of the diphenylmercury taken for the reaction. The 0.8 g (16%) of diphenylmercury that did not enter into the reaction was recovered from the mother liquor after the phenylmercury chloride had been separated out; the recovered substance had a m.p. of 125° after recrystallization from acetone.

Diphenylmercury and chloroform. 1.0 g of diphenylmercury in 15 ml of chloroform was irradiated for 6 hours. The solution turned yellow, with a deposit of phenylmercury chloride and a small amount of metallic mercury on the bottom of the reaction vessel. The deposit was filtered out and recrystallized from acetone. A total of 0.5 g (57% of the diphenylmercury used) of phenylmercury chloride, with a m.p. of 257°, was recovered; it caused no depression of the melting point when mixed with the pure product. The filtrate was driven off over a water bath and nitrated. This yielded m-dinitrobenzene, with a m.p. of 90°. After steam distillation of the residue, we obtained hexachloroethane,

which had a m.p. of 186° in a sealed capillary after refining by subliming; it caused no depression of the melting point when mixed with pure hexachloroethane. After the hexachloroethane had been isolated from the residue, the diphenylmercury that had not entered into the reaction was recovered by extraction with alcohol: 0.4 g (40%), with a m.p. of 124°.

Diphenylmercury and dichloroethane. 1.0 g of diphenylmercury in 10 ml of dichloroethane was irradiated for 6 hours. Crystals of phenylmercury chloride and a small amount of mercury settled out of the solution. The 0.35 g (41% of the solution in terms of the diphenylmercury used) of diphenylmercury chloride that was filtered out had a m.p. of 255°; it caused no depression of the melting point when mixed with the pure substance. The filtrate was steam distilled and nitrated. The nitro compound synthesized had a melting point of 90°. The residue after steam distillation contained 0.52 g (52% of the amount placed in the reaction) of diphenylmercury, which had a m.p. of 125° after recrystallization.

Diphenylmercury and tetrachloroethane. A solution of 2.0 g of diphenylmercury in 15 ml of tetrachloroethane was irradiated for 10 hours. Crystals of phenylmercury chloride and a small amount of mercury settled out of the solution. Recrystallization from acetone yielded 1.1 g (63% of the diphenylmercury initially taken) of a substance with a m.p. of 257°; it caused no depression of the melting point when mixed with pure phenylmercury chloride. The filtrate was steam distilled and the distillate then nitrated. The nitro product isolated had a melting point of 90°. After the solvent had been driven off, we recovered from the residue 0.58 g of diphenylmercury (29% of the amount initially taken), m.p. 125° after recrystallization from alcohol.

Diphenylmercury and hexachloroethane. 2.0 g of diphenylmercury and 2.0 g of hexachloroethane were dissolved in 15 ml of benzene. After 10 hours of irradiation, crystals of phenylmercury chloride settled out of the solution; they were filtered out and recrystallized from acetone. This yielded 0.5 g of a substance with a m.p. of 256° (28% of the diphenylmercury initially taken); it caused no depression of the melting point when mixed with pure phenylmercury chloride.

SUMMARY

1. A solution of diphenylmercury in methanol is decomposed into mercury, benzene, and formaldehyde by irradiation with light.

2. Irradiation of a solution of diphenylmercury in CCl_4 yields phenylmercury chloride, chlorobenzene, and hexachloroethane.

3. Irradiation of a solution of diphenylmercury in chloroform yields phenylmercury chloride, benzene, and hexachloroethane.

4. The phenyl radical liberated by photolysis reacts with the hydrogen, but not with the chlorine in the following solvents: CHCl_3 , $\text{C}_2\text{H}_2\text{Cl}_4$, $\text{C}_2\text{H}_4\text{Cl}_2$.

The $\text{C}_6\text{H}_5\text{Hg}$ radical breaks an atom of chlorine away from the solvent. The reaction is accompanied by the liberation of small amounts of metallic mercury.

5. The action of light upon a benzene solution of diphenylmercury and hexachloroethane results in the formation of phenylmercury chloride.

6. The equations of the photochemical reactions occurring in this first photolysis of diphenylmercury are set forth.

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RESEARCH IN THE ANTHRAQUINONE SERIES

XIV. THE α , α' -DISULFINIC ACIDS OF ANTHRAQUINONE*

V. V. Kozlov and D. D. Stolin

Little research has been done on the sulfinic acids of the aromatic hydrocarbons. In the anthraquinone series, it is not so long ago that the α - and β -sulfinic acids of anthraquinone were synthesized [1]. We resolved to synthesize the 1,5-, 1,8-, and 1,4-disulfinic acids of anthraquinone, which we needed for the conversions to be described in forthcoming reports. There were two possible ways of synthesizing them, both tried out in the synthesis of monosulfinic acids of anthraquinone [2]: a) reacting an alcohol-alkali solution of anthraquinonesulfenic acid with potassium ferricyanide; b) reducing anthraquinone sulfochloride with alkali sulfides. We chose the second, easier method, which is based upon the following reaction:



Reduction of an aqueous suspension of 1,5-anthraquinone sulfochloride by sodium sulfide synthesized the 1,5-disulfinic acid with a yield of 83.5% of theory. The substance crystallizes out of aqueous methanol as small, light-pink prisms, with a m.p. of 218-220° (with decomposition). The substance is readily soluble in hot water, less so in cold, and hardly soluble in dilute mineral acids. It is soluble in alcohols, acetone, and acetic acid, and is practically insoluble in the hydrocarbons. 1,8-Anthraquinonedisulfinic acid was similarly synthesized with a yield of 77.5% of theory. This substance is more soluble in water than is the 1,5-isomer. It crystallizes best from alcohol acidulated with hydrochloric acid, as small, light-yellow platelets, with a m.p. of 171° (with decomposition). The same method was used to synthesize 1,4-anthraquinonedisulfinic acid, with a yield that was 90.06% of theory. This substance is even more soluble in water than are the 1,5- and 1,8-isomers; it crystallizes out of alcohol saturated with anhydrous hydrogen chloride as tiny needles, with a m.p. of 154° (with decomposition). The interesting relationship between the order of magnitude of the melting points and solubilities of the synthesized disulfinic acids and those of the corresponding anthraquinone-disulfonic acids [3] is shown in Table 1.

The same solubility pattern is seen in the salts of these acids, the solubility of salts of the 1,8-disulfinic acid being lower than that of salts of the 1,5-disulfinic acid, which is fully analogous to the pattern for the corresponding salts of the anthraquinonedisulfonic acids.

* See J. Gen Chem. USSR, 18, 2094 (1948), for Report XIII.

Table 1

Comparative Characteristics of Anthraquinonedisulfonic and -disulfinic Acids

Acid	Melting point	Solubility in water at 20°
1,5-disulfonic acid	312°	1 part per 1.5 parts H ₂ O
1,8-disulfonic acid	293.5	1 part per 1.4 parts H ₂ O
1,4-disulfonic acid [4].....	262	1 part per 0.5 parts H ₂ O
1,5-disulfinic acid	220	1 part per 5.0 parts H ₂ O
1,8-disulfinic acid	171	1 part per 1.5 parts H ₂ O
1,4-disulfinic acid	154	very highly soluble

EXPERIMENTAL

Synthesis of free 1,5-anthraquinonedisulfinic acid. 4 g of 1,5-anthraquinonedisulfochloride, with a m.p. of 270.5°, prepared by heating the potassium salt of 1,5-anthraquinonedisulfonic acid with PCl₅, is carefully stirred with 8 ml of water in a glass, cooled externally to 5-10°. To the suspension thus prepared there is added, with stirring, a solution of 4.8 g of crystalline sodium sulfide in 6 g of water. The reaction is rapid and is accompanied by an increase in the temperature of the medium, which is kept at 40°. After stirring has been continued for 30 minutes, the dark-brown solution is filtered to remove the precipitated sulfur and then acidulated with hydrochloric acid until it gives an acid reaction with Congo paper. The precipitate that is thrown down is filtered out and twice recrystallized from 10% ammonia by acid, after which it is filtered out, washed on the filter with a small amount of cold water and then with alcohol, and finally desiccated in a vacuum exsiccator. This yielded 2.8 g of the product, or 83.5% of theory, in terms of the disulfinic acid.

0.1608 g substance: 0.2192 g BaSO₄ (Carius method).

Found %: S 18.65.

C₁₄H₈O₂(SO₂H)₂. Calculated %: S 19.04.

0.1002 g substance: 0.1994 g CO₂; 0.0218 g H₂O.

Found %: C 49.72; H 2.41.

C₁₄H₈O₆S₂. Calculated %: C 50.0; H 2.38.

The dry anhydrous acid is hygroscopic, but does not deliquesce in air. It absorbs as much as 4 moles of water upon long standing in air.

0.1002 g of dry substance absorbs 0.0208 g of water.

Found %: H₂O 17.19.

C₁₄H₈O₂(SO₂H)₂·4H₂O. Calculated %: H₂O 17.64.

One part of the acid dissolves in 5 parts of water at 20°. An aqueous solution of the acid, slightly acidulated with sulfuric acid, gradually consumes a 0.1N permanganate solution, owing to the oxidation of the sulfinic groups to sulfo groups. The acid is readily titrated with a 0.1N solution of sodium hydroxide with methyl red as an indicator.

0.0908 g substance: consumed 5.5 ml of 0.1N NaOH.

Found: equiv. 166

C₁₄H₈O₂(SO₂H)₂. Calculated: equiv. 168.

Table 2

Brief Description of the Salts of 1,5-Anthraquinonedisulfinic Acid

Formula	Description	Solubility of the anhydrous salt in water	
		20°	100°
$C_{14}H_6O_2(SO_2)_2Cu \cdot 2H_2O \dots$	Yellow leaflets from water	1:75	1:25
$C_{14}H_6O_2(SO_2)_2Ni \cdot 2H_2O \dots$	Yellow leaflets from water	1:125	1:56
$C_{14}H_6O_2(SO_2)_2Pb \cdot H_2O \dots$	Light-yellow leaflets from water	insoluble	very poorly soluble
$C_{14}H_6O_2(SO_2)_2Ba \dots \dots \dots$	Yellow needles from alcohol		insoluble
$C_{14}H_6O_2(SO_2)_2Zn \cdot 5H_2O \dots$	Yellow needles from water	1:98	1: 30

Salts of 1,5-anthraquinonedisulfinic acid. The potassium, sodium, ammonium, and silver salts are very highly soluble in water. The magnesium and calcium salts are readily soluble in water. The salts listed in Table 2 were synthesized by mixing equivalent quantities of 0.1N solutions of the diammonium salt of 1,5-anthraquinonedisulfinic acid with various mineral salts. The solutions of the ammonium salt of the acid were prepared by neutralizing a solution of the free acid with ammonia, followed by removing the slight excess of the latter by boiling the ensuing solution.

Synthesis of the double mercury-chlorine salt of 1,5-anthraquinonedisulfinic acid. A solution of 0.84 g of 1,5-anthraquinonedisulfinic acid in 50 ml of 0.1N sodium hydroxide is slowly poured, at room temperature into a boiling solution of 2.75 g of mercuric chloride in 8 ml of water. A yellow amorphous precipitate is thrown down at once; it is filtered out, washed with hot water and then with alcohol, and dried in an exsiccator. This yields 1.5 g of product, or 74.5% of theory in terms of the mercury-chlorine salt of 1,5-anthraquinone-disulfinic acid. The substance contains mercury, chlorine, and sulfur. The substance is insoluble in all organic solvents, is infusible up to 340°, but breaks down, yielding sublimed $HgCl_2$ and yellow crystals, with a m.p. of 285°, which proved to be anthraquinone. The substance is soluble in concentrated sulfuric acid.

Determination of mercury (Koshkin method [5]).

0.1439 g of substance after decomposition with sulfuric acid, it was dissolved in 100 ml water. In titration, 1 ml of the solution required 0.610 ml of a 0.1N solution of KI ($T_{KI} = 0.001178$ g Hg).

Found %: Hg 49.62.

$C_{14}H_6O_6S_2 \cdot Hg_2Cl_2$. Calculated %: Hg 49.75.

0.1002 g substance : 0.0363 g $AgCl$.

Found %: Cl 8.96.

$C_{14}H_6O_6S_2 \cdot Hg_2Cl_2$. Calculated %: Cl 8.81.

0.1002 g substance: 0.0554 g $BaSO_4$.

Found %: S 7.59.

$C_{14}H_6O_6S_2 \cdot Hg_2Cl_2$. Calculated %: S 7.95.

Synthesis of 1,8-anthraquinonedisulfinic acid. 4 g of 1,8-anthraquinone disulfochloride with a m.p. of 221.5°, prepared by heating the dipotassium salt of 1,8-anthraquinonedisulfonic acid with PCl_5 , is treated with a solution of sodium sulfide, as was done with the 1,5-anthraquinone disulfochloride mentioned above. After 30 minutes of stirring at 40°, the reaction mass is filtered out to remove the sulfur and then acidulated with 100 ml of concentrated hydrochloric acid (sp. gr 1.19). With lower acidity and smaller quantity of the hydrochloric acid, the disulfinic acid in solution does not separate out, owing to its high solubility in water. 1,8-anthraquinonedisulfinic acid separates out as a tarry, dirty-yellow mass (2.6 g or 77.5% of theory). The crude disulfinic acid is washed on the filter with a very small quantity of ice water and then with alcohol, and dried over P_2O_5 in a vacuum exsiccator.

Because of the high solubility of the isolated disulfinic acid in water, alcohols, acetone, and acetic acid, its crystallization entails considerable losses. The substance is almost insoluble in hydrocarbons.

0.2224 g substance: loss in wt. at 150° - 0.01115 g.

Found %: H_2O 5.21.

$\text{C}_{14}\text{H}_8\text{O}_2(\text{SO}_2\text{H})_2 \cdot \text{H}_2\text{O}$. Calculated %: H_2O 5.08.

0.1122 g dry substance: 0.1551 g BaSO_4 .

Found %: S 18.95.

$\text{C}_{14}\text{H}_8\text{O}_2(\text{SO}_2\text{H})_2$. Calculated %: S 19.04.

0.0908 g substance: 0.1661 g CO_2 : 0.0207 g H_2O .

Found %: C 49.92; H 2.49.

$\text{C}_{14}\text{H}_8\text{O}_6\text{S}_2$. Calculated %: C 50.0; H 2.38.

The acid, desiccated over P_2O_5 (it does not lose its water of crystallization!), is extremely hygroscopic in air, rapidly deliquescing into a formless, semi-liquid mass. An aqueous solution of the substance, slightly acidulated with sulfuric acid, gradually consumes a 0.1N solution of permanganate in the cold owing to the oxidation of the sulfinic groups to sulfo groups. The acid is readily titrated with a 0.1N solution of sodium hydroxide, using methyl red as an indicator:

0.0772 g substance: 4.56 ml of 0.1N NaOH consumed.

Found : equiv. 167

$\text{C}_{14}\text{H}_8\text{O}_2(\text{SO}_2\text{H})_2$. Calculated : equiv. 168

Salts of 1,8-anthraquinonedisulfinic acid. The potassium, sodium, ammonium, silver, and magnesium salts are readily soluble in water. The salts listed below were synthesized by mixing equivalent quantities of 0.1N solutions of diammonium of 1,8-anthraquinonedisulfinate with various mineral salts. The solutions of the ammonium salt were prepared in the same manner as the corresponding salt of the 1,5-disulfinic acid.

A brief description of these salts is given in Table 3.

Synthesis of 1,4-anthraquinonedisulfinic acid. 2 g of 1,4-anthraquinone disulfochloride, with a m.p. of 239°, synthesized by heating the double sodium salt of 1,4-anthraquinonedisulfonic acid with PCl_5 [4], is treated with a solution of sodium sulfide as described above for the 1,5- and 1,8-anthraquinone disulfochlorides. After having been stirred for 30 minutes at 40°, the reaction mass is filtered to remove the sulfur, strongly chilled to 2-5°, acidulated with 35 ml of concentrated HCl (sp. gr 1.19), and saturated with gaseous hydrogen

Table 3
Brief Description of the Salts of 1,8-Anthraquinonedisulfinic Acid

Formula	Description	Solubility of the anhydrous salt in water	
		at 20°	at 100°
$C_{14}H_6O_2(SO_2)_2Cu \cdot 3H_2O\dots$	Yellow platelets from alcohol or water	1:125	1:115
$C_{14}H_6O_2(SO_2)_2Ni \cdot 5H_2O\dots$	Lamellae from water or alcohol	1:340	1:165
$C_{14}H_6O_2(SO_2)_2Pb \cdot H_2O\dots$	Platelets from water or aqueous acetic acid	1:650	1:275
$C_{14}H_6O_2(SO_2)_2Ca \cdot 4H_2O\dots$	Microscopic crystals from water	1:850	1:68
$C_{14}H_6O_2(SO_2)_2Ba \cdot 2H_2O\dots$	Platelets from water or aqueous acetic acid	1:840	1:145
$C_{14}H_6O_2(SO_2)_2Zn \cdot 4H_2O\dots$	Microscopic crystals from water	1:200	1:95

chloride for 15-30 minutes. Contrary to the 1,8-disulfinic acid, and even more so to the 1,5-anthraquinonedisulfinic acid, this last disulfinic acid does not separate out even when the solution is strongly acidified. For full precipitation the solution must be completely saturated with hydrogen chloride while chilled. The 1,4-disulfinic acid separates out gradually as sand-colored tiny grains, which gradually coalesce into a compact mass. If this mass is exposed to the air for some time at room temperature, the acid again enters into solution in the hydrochloric acid. The synthesized disulfinic acid is filtered out and dried in a high vacuum over sodium hydroxide. Yield: 1.51 g, or 90.06% of theory. The substance is perfectly soluble in water, alcohol, and acetone, partially soluble in xylene, and nearly insoluble in other hydrocarbons.

0.0654 g substance: 0.0919 g $BaSO_4$.

Found %: S 19.19.

$C_{14}H_6O_2(SO_2H)_2$. Calculated %: S 19.04.

5.522 mg substance: 10.226 mg CO_2 ; 1.200 mg H_2O .

Found %: C 50.5; H 2.41.

$C_{14}H_8O_6S_2$. Calculated %: C 50.0; H 2.38.

Most of the salts of 1,4-anthraquinonedisulfinic acid are very easily soluble in water.

SUMMARY

The 1,5-, 1,8-, and 1,4-anthraquinonedisulfinic acids have been synthesized, and their salts investigated.

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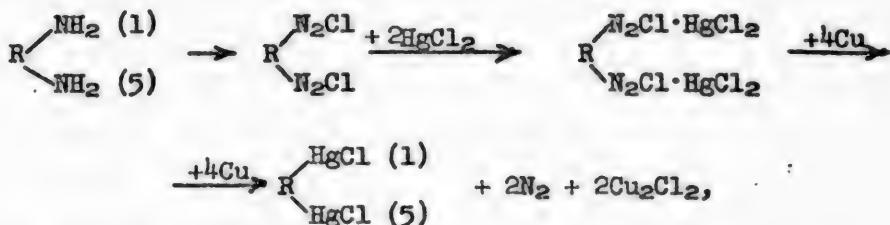
RESEARCH IN THE ANTHRAQUINONE SERIES

XV. THE ASYMMETRICAL 1,5-MERCURY COMPOUNDS OF ANTHRAQUINONE

V. V. Kozlov and D. D. Stolin

Having synthesized and studied the properties of α -anthraquinonylmercury [1], we undertook the synthesis of the asymmetrical α - α' -mercury compounds of anthraquinone, the formation of which could be assumed with safety as intermediate products in the sulfonation of anthraquinone in the presence of mercury to the 1,5- and 1,8-anthraquinonedisulfonic acids. A few compounds of the aromatic series containing two mercury groups attached to two carbon atoms of a single core are known, but mercury compounds of that sort are wholly unknown in the anthraquinone series.

Having achieved quite satisfactory results in applying the method developed by A.N. Nesmeyanov [2] to the monoaminoanthraquinones [1], we employed the same method for the diaminoanthraquinones, as follows:

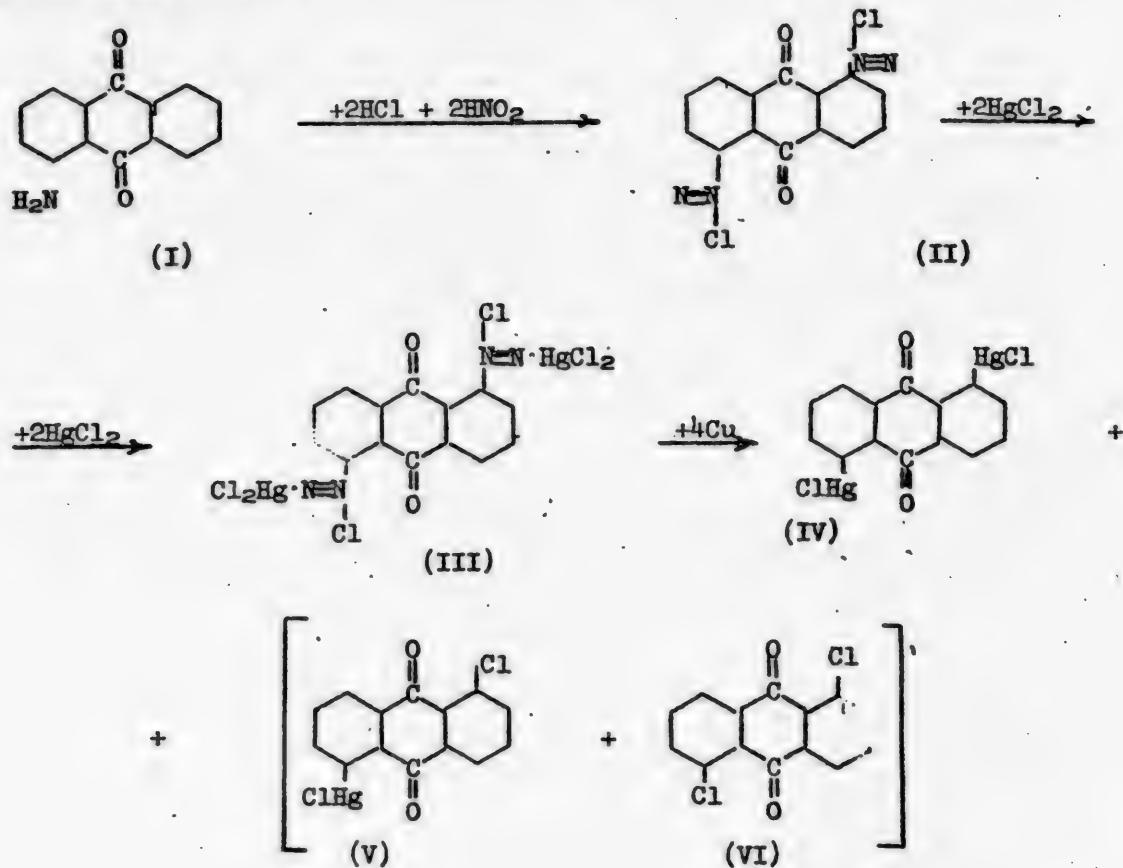


where R = the anthraquinone core.

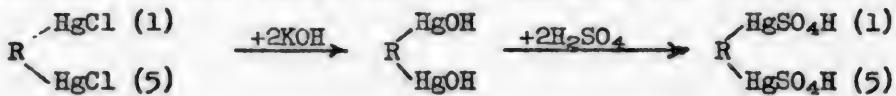
The reaction of solutions of mercuric chloride in hydrochloric acid with diazotized 1,5-diaminoanthraquinone [3] resulted in the synthesis of a double chloride of mercury and bisdiazonium, with a yield of 47% of theory. Decomposition of this salt by copper powder in acetone yielded the product we required as 1,5-anthraquinonemercury chloride, with a yield of as high as 30%. This substance is practically insoluble in such organic solvents as alcohols, benzene, xylol, acetone, anisole, phenol, or pyridine, but it is readily soluble in the cold in weak oleum, coloring the solution an intense yellow, and somewhat less soluble in concentrated sulfuric acid (at 40-50°). The substance can be purified without visible decomposition by pouring the sulfuric acid solution into water. The substance decomposes at 320-330° (it does not fuse).

Synthesis of this compound is accompanied by the formation of such decomposition products as 1-chloro-anthraquinonemercury-5-chloride and 1,5-dichloro-anthraquinone mixed with metallic mercury. The overall picture of the

bis diazonium conversion of 1,5-diaminoanthraquinone in A.N.Nesmeyanov's diazo reaction is as follows:

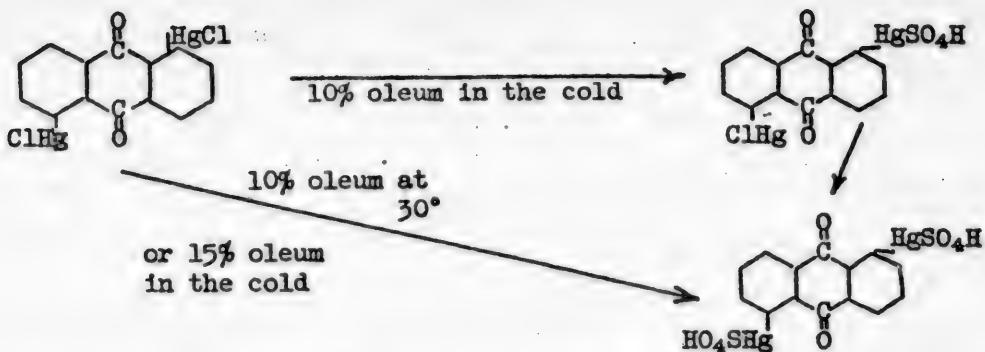


The principal reaction product, 1,5-anthraquinonylmercury chloride, is converted into the 1,5-dihydroxide of mercury, and the latter yields 1,5-anthraquinonylmercury sulfate when acted on by sulfuric acid, as follows:



The latter compound is a light-yellow powder that is insoluble in organic solvents and can be purified by recrystallization by water from a solution in weak oleum. The 1,5-anthraquinonylmercury chloride dissolves into the monohydrate when heated slightly, being recovered later unchanged. Its solubility is made easier by using oleum: 5% oleum, while not causing any visible decomposition of the substance, precipitates it unchanged when poured into water. As indicated by one of the present authors for anthraquinonylmercury chloride [1], 10% oleum effects the substitution of a hydrochloric-acid group by a sulfuric acid group. In the cold, however, only a single group is replaced, the substitution of both groups by 10% oleum requiring a somewhat higher temperature (30°). Stronger oleum (15-18% SO₃) effects this substitution at low temperature as well. These transformations are shown in the following diagram:

Increasing the oleum concentration to 30-40% SO₃ results in decomposition



of the mercury compound in the cold (and does this rapidly when slightly heated), forming an anthraquinone - disulfonic acid. When 1,5-anthraquinonylmercury sulphate is reacted at 140° with 10% oleum for 30 minutes, consuming 150% of theory of the latter, we find that as much as 25.5% of 1,5-anthraquinone-disulfonic acid is formed, it separating out of the solution as a dipotassium salt. The latter is formed by the action of dichloroanthraquinone chlorate, with a m.p. of 241-242°; it causes no depression when fused in a test sample mixed with 1,5-dichloroanthraquinone. The unchanged 1,5-anthraquinonylmercury sulfate left is 70.4% of theory. The action of an amount of 25% oleum that is 150% of theory upon 1,5-anthraquinonylmercury sulfate for 1.5 hours at 140° results in the formation of 1,5-anthraquinonedisulfonic acid (90% of theory), anthraquinone (5%) and anthraquinonehydroxysulfonic acid (traces).

Thus, the action of oleum upon 1,5-anthraquinonylmercury sulfate results in the formation of the same products as are usually detected in the sulfo mass after the sulfonation of anthraquinone in the presence of mercury (together with the 1,8 isomer). As has already been stated by us in the case of α -anthraquinonylmercury sulfate [1]; the formation of 1,5-anthraquinonedisulfonic acid from the mercury compound takes place much more rapidly than in the direct disulfonation of anthraquinone. The complete replacement of the mercury groups by the sulfo radicals occurs at milder conditions of temperature as well as of concentration of the sulfonating agent. It is noteworthy that the amount of free anthraquinone found by us when 25% oleum is allowed to act upon 1,5-anthraquinonylmercury sulfate corresponds to the amount of "recovered" anthraquinone usually remaining behind during the direct disulfonation of anthraquinone in the presence of mercury. This formation of anthraquinone in our instance is probably the result of a displacement of the reaction equilibrium, according to the following equation:



EXPERIMENTAL.

Synthesis of the double salt of 1,5-anthraquinonylbis diazonium chloride and mercuric chloride. 2.38 g of 1,5-diaminoanthraquinone, with a m.p. of 313-314°, is triturated with 2 ml of glycerol to a thin paste, mixed with 20 ml of concentrated sulfuric acid, and heated to boiling for 30 minutes. The suspension of the sulfate is cooled to 40-50° and diazotized with 30 ml of a 20% solution of NaNO₂. This diazo solution is allowed to stand for two hours, after which the impurities are filtered out, and the solution is added to a solution consisting of 8.7 g of yellow mercuric oxide in 50 ml of 30% HCl and 50 ml of water. A crystalline precipitate is immediately thrown down in the shape of tiny light-pink, silky needles. After being allowed to stand for 2-3 hours, the precipitate is filtered out, washed with ice water and then with alcohol, and dried in a vacuum exsiccator over P₂O₅. Yield: 4.2 g or 47% of theory, based on the initial

diaminanthraquinone. The substance is soluble in cold water and readily soluble in hot water, from which it can be recrystallized; it is also soluble in alcohols and acetone, but insoluble in hydrocarbons and dilute acids. The substance slowly darkens when exposed to light and decomposes without melting at 330°. Analysis of the diazo salt by decomposition with 55% sulfuric acid and potassium bichromate [4] and recovery of the isolated diazo acid in a Lunge azotometer over potassium hydroxide yielded the following results:

0.6157 g substance: 36.5 ml N₂ (17°, 744 mm).

Found %: N 6.75.

C₁₄H₆O₂N₄Cl₆Hg₂. Calculated %: N 6.39.

Kjeldahl nitrogen determination [5]: 0.1274 g of substance: after decomposition in sulfuric acid, dissolved in 100 ml water. 0.49 ml of 0.01N KI solution required to titrate 1 ml of solution (T_{KI} = 0.001178 g Hg).

Found %: Hg 44.8.

C₁₄H₆O₂N₄Cl₆Hg₂. Calculated %: Hg 45.66.

Synthesis of 1,5-anthraquinonylmercury chloride. 8.7 g of the anhydrous double mercury salt is suspended in 50 ml of anhydrous acetone and 2.5 g of copper powder is added to the suspension at 20-30°, with uninterrupted stirring. Decomposition is rapid, but the reaction mixture has to be set aside overnight, for decomposition to be complete. Then the mass is filtered, and the residue thoroughly washed on the filter with hot alcohol. The filtrate is clarified with activated charcoal and filtered while hot, and the solvent is driven off until the volume is 5-7 ml. Upon cooling, a crystalline deposit settles out of the solution; this deposit is filtered out, washed with a small quantity of cold alcohol, and desiccated. Weight: 9.8 g. After repeated recrystallization from alcohol, the substance fuses indistinctly within the range of 136-144°. The substance contains mercury and a halogen and constitutes a mixture of various substances, detectable as crystals under the microscope. After another washing with alcohol, the product is subjected to prolonged extraction (for about 40 hours) with boiling xylene until the extract is colorless. The xylene extract is boiled with charcoal and filtered out, and the solvent is driven off until the remaining volume is 5-6 ml. The deposit that settles out upon cooling is filtered out, washed with a small amount of cold xylene, and desiccated in a vacuum exsiccator over paraffin shavings. Weight: 9.6 g. After recrystallization from xylene the substance again contains Hg and Cl, fuses at 230-240°, and is a mixture of substances: Crystallization from various solvents does not yield a substance with a more or less sharp melting point, though the substance fuses without visible decomposition. Prolonged cold extraction (for 5 days) of the product with absolute alcohol yields a substance that crystallizes in fine needles, with a m.p. of 243°. The substance contains chlorine but no mercury and is 1,5-dichloroanthraquinone. After extraction with xylene, the residue, a dark-gray amorphous mass, is visibly impregnated with metallic mercury. This residue is treated with 30% nitric acid in the cold for 12 hours to remove the mercury and copper salts. The color of the product changes from gray to yellow. The precipitate is filtered out and washed with water until its reaction is neutral; then it is washed with hot alcohol to remove any possible traces of anthraquinone and desiccated at 110-120°. Weight: 1.85 g or 27% of theory, based on the initial mercury salt. It exhibits a characteristic blackening when treated with caustic alkalies or ammonia. The substance contains mercury and chlorine.

0.2617 g of substance: 100 ml of water: titration of 1 ml required 1.32 ml of 0.01N KI (T_{KI} = 0.001178 g Hg).

Found %: Hg 59.82
 $C_{14}H_6O_2Hg_2Cl_2$. Calculated %: Hg 59.08.
0.2102 g substance: 0.0683 g AgCl.

Found %: Cl 10.72.
 $C_{14}H_6O_2Hg_2Cl_2$. Calculated %: Cl 10.48.
0.2874 g substance: 0.2566 g CO₂; 0.0216 g H₂O.
Found %: C 24.41; H 1.02.
 $C_{14}H_6O_2Hg_2Cl_2$. Calculated %: C 24.81; H 0.88.

Synthesis of anthraquinonyl-1,5-mercury hydroxide. 1.0 g of 1,5-anthraquinonylmercury chloride is suspended in 60 ml of anhydrous methanol and then heated for 6 hours over a water bath in a flask fitted with a reflux condenser. The alcoholic solution turns dark brown, and the precipitate changes from yellow to blackish-brown. The precipitate is filtered out, washed with hot methanol, water, and alcohol again, and then dried in a vacuum exsiccator.

A small quantity of the substance dissolves in an alcohol-alkaline solution. The principal reaction product, a blackish-brown amorphous powder, contains no chlorine, but does contain mercury; it does not fuse, but is soluble in ordinary solvents. The yield of crude product is 0.85 g or 90.42% of theory, based on anthraquinonylmercury hydroxide.

0.1588 g of substance: 100 ml water; 1 ml required 0.82 ml of 0.01N KI (T_{KI} = 0.001175 g Hg).

Found %: Hg 62.75.
0.1502 g substance: 0.1433 g CO₂; 0.018 g H₂O.
Found %: C 26.02; H 1.31.
 $C_{14}H_6O_2(HgOH)_2$. Calculated %: Hg 62.5; C 26.25; H 1.25.

Synthesis of 1,5-anthraquinonylmercury sulfate. 1) 0.5 g of anthraquinonyl-1,5-mercury hydroxide is finely pulverized and poured, with stirring, into 10 ml of sulfuric acid (sp.gr. 1.84) chilled to 0°. The substance dissolves quickly, turning the solution reddish brown. The solution, which is perfectly transparent after the undissolved particles have been filtered out, is cautiously diluted with water a drop at a time until its volume has been tripled. The precipitated deposit is filtered out, washed with water and then with alcohol, and dried in a vacuum exsiccator. Yield: 0.65 g or 95.5% of theory, based on 1,5-anthraquinonylmercury sulfate. The substance contains mercury and sulfur; it is infusible and insoluble in organic solvents or concentrated sulfuric acid, but is soluble in weak oleum, from which it may be purified by decantation over ice.

0.1481 g of substance: 100 ml of water: 1 ml requires 0.59 ml of 0.01N KI (T_{KI} = 0.001175 g Hg).

Found %: Hg 50.04.
0.1668 g substance: 0.0965 g BaSO₄.
Found %: S 7.89.
 $C_{14}H_6O_2(HgSO_4H)_2$. Calculated %: S 8.00; Hg 50.00.

2) 1.0 g of 1,5-anthraquinonylmercury chloride, with a decomp. temp. of 330°, is finely powdered and suspended in 25 ml of 5% oleum at 15° in a tightly sealed flask. After 1.5-2 hours, when a perfectly homogeneous mass has been produced, it is filtered (preferably in a closed system) through an acidproof filter directly over ice. The yellow deposit that settles is filtered out and washed, first with cold and then with hot water. This yields 0.9 g of a substance with a decomp. temp. of 330°. The substance contains mercury and chlorine

and is wholly identical with the initial substance: 1,5-anthraquinonylmercury chloride.

3) 1.0 g of 1,5-anthraquinonylmercury chloride is dissolved as before in 25 g of 10% oleum at 15°. When the solution is decanted over ice, a gray substance separates out that is insoluble in solvents, but dissolves in sulfuric acid when slightly heated. The substance does not fuse, but decomposes at 350°; it contains mercury, chlorine, and sulfur. The yield is 0.94 g or 86.2% of theory, based on the mixed salt: 1,5-anthraquinonylmercury chloride sulfate.

0.2412 g of substance: 100 ml of water; 1 ml of solution required
1.1 ml 0.01N KI solution ($T_{KI} = 0.001174$ g Hg).

Found %: Hg 54.28.

0.2018 g substance: 0.0400 g AgCl.

Found %: Cl 4.91.

0.2016 g substance: 0.0613 g BaSO₄.

Found %: S 4.18.

0.2112 g substance: 0.1758 g CO₂; 0.0177 g H₂O.

Found %: C 22.52; H 0.98

C₁₄H₆O₂·HgCl₁·HgSO₄H. Calculated %: Hg 54.16; Cl 4.8; S 4.33 C 22.74; H 0.94.

4) 1.0 g of 1,5-anthraquinonylmercury chloride is dissolved as before in 25 g of 10% oleum at 30° for 6 hours. After the prepared and filtered solution has been decanted over ice, a dark substance separates out, which is insoluble in solvents or concentrated sulfuric acid, but is soluble in weak oleum, from which it can be purified by decantation into water. The substance is infusible and contains sulfur and mercury. Yield: 1.21 g or 94.5% of theory, based on 1,5-anthraquinonylmercury sulfate.

0.1528 g of substance: 100 ml of water; 1 ml of solution
required 0.61 ml of 0.01N KI solution ($T_{KI} = 0.001174$ g Hg).

Found %: Hg 49.01.

0.2622 g substance: 0.1415 g BaSO₄.

Found %: S 7.41.

0.3112 g substance: 0.2181 g CO₂; 0.0270 g H₂O.

Found %: C 19.11; H 0.96.

C₁₄H₆O₂(HgSO₄H)₂. Calculated %: Hg 50.0; S 8.0; C 21.0; H 1.0.

5) 1.0 g of 1,5-anthraquinonylmercury chloride is treated as before with 20 g of 15% oleum for 6 hours in the cold. The product that is separated out by decantation into water is washed with cold and hot water, and then with warm acetic acid (to remove the traces of anthraquinone), and then again with water. The yield is 1.1 g of substance, or 85.9% of theory, based on 1,5-anthraquinonylmercury sulfate. The properties of the substance resemble those of the substance synthesized in the experiment with 10% oleum at 30°.

0.1618 g of substance: 100 ml of water; 1 ml of solution required
0.66 ml of 0.01N KI solution ($T_{KI} = 0.001174$ g Hg).

Found %: Hg 49.71.

0.3008 g substance: 0.1729 g BaSO₄.

Found %: S 7.88.

C₁₄H₆O₂(HgSO₄H)₂. Calculated %: Hg 50.0; S 8.0.

Sulfonation of 1,5-anthraquinonylmercury sulfate. 1) 4 g of the substance

is sulfonated with 12 g of 10% oleum at 140° for 30 minutes. 0.56 g of the disulfonic salt is salted out of the aqueous solution by potassium chloride, its chloroanthraquinone fusing at 241° and causing no depression when fused in a mixed test sample with pure 1,5-dichloroanthraquinone. The residue of 2.8 g, which is water-insoluble, is unchanged 1,5-anthraquinonylmercury sulfate.

2) 4 g of the substance is sulfonated by 4.8 g of 25% oleum for 1.5 hours at 140°. The water insoluble residue contains no mercury and is anthraquinone (0.05 g) with traces of hydroxy compounds (slightly colored by caustic alkalies). 2 g of the dipotassium salt of 1,5-anthraquinonedisulfonic acid is salted out of an acid solution, its chloroanthraquinone fusing at 242° and exhibiting no depression when fused in a mixed test sample with pure 1,5-dichloroanthraquinone.

SUMMARY

1. 1,5-Anthraquinonylmercury chloride and its derivative: 1,5-anthraquinonyl sulfate have been synthesized by the diazotization method of A.N.Nesmeyanov.

2. It has been established that 1,5-anthraquinonedisulfonic acid is formed by the action of oleum upon 1,5-anthraquinonyl sulfate. Its formation occurs at a faster rate, a lower temperature, and a lower concentration of oleum than the formation of the sulfoacids in the disulfonation of anthraquinone with mercury.

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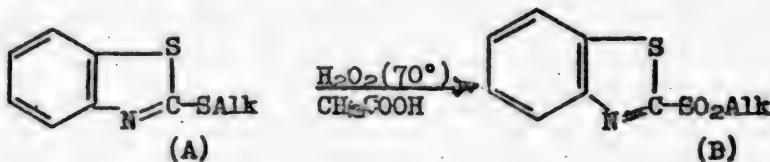
OXIDATION OF SOME SULFIDES OF THE BENZOTHIAZOLE SERIES

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As we know from the literature [1], mercaptobenzthiazole condenses readily with substances that contain a mobile halogen atom, forming the corresponding sulfides. This reaction was found to be applicable to alkyl halides, which enables us to synthesize various alkylbenzthiazolyl sulfides (A) readily by heating equimolecular amounts of the potassium salt of mercaptobenzthiazole with the respective alkyl halide in an absolute alcohol solution.

This availability of the most diverse sulfides of the benzthiazole series impelled us to investigate the problem of their oxidation by hydrogen peroxide. It was found that alkylbenzthiazolyl sulfides readily form the corresponding alkylbenzthiazolyl sulfones (B) when oxidized by twice the amount of hydrogen peroxide in acetic acid at 60-70°.



Some Alkylbenzthiazole Sulfides and Sulfones

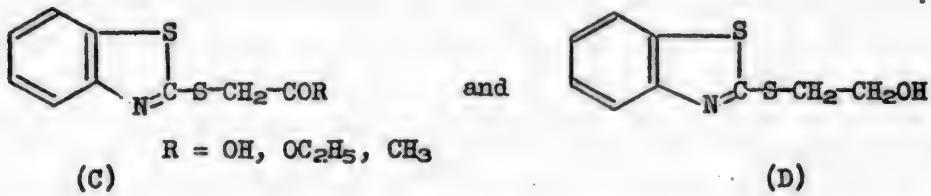
Name	Temperature		Yield %	Found (%)		Computed (%)	
	M.p.	B.p.(mm)		N	S	N	S
Cyclohexylbenzthiazolyl-2 sulfide	47°	183-186°	82	5.73	25.46	5.62	25.72
Benzylbenzthiazolyl-2-sulfide.	40-41	168-172	85	-	-	-	-
β-Phenylethylbenzthiazolyl-2-sulfide	24	143-146	78	5.23	23.64	5.17	23.64
Cyclohexylbenzthiazolyl-2 sulfone	117-119	-	75	5.05	23.11	4.98	22.79
Benzylbenzthiazolyl-2-sulfone.	112-114	-	68	4.98	22.10	4.84	21.83
β-Phenylethylbenzthiazolyl-2 sulfone.	83-84	-	69	4.73	20.88	4.63	21.14

This general method of oxidizing the sulfides to sulfones [2] yields quite satisfactory results in the alkylbenzthiazolyl series. In the experimental

section below we give the general methods for synthesizing alkylbenzthiazolyl sulfides and their oxidation to the respective sulfones. The constants and yields of some sulfides and sulfones are listed in the table above.

Oxidation of the alkylbenzthiazolyl sulfides by hydrogen peroxide (1 mole) under milder conditions ought to result in the formation of the corresponding sulfoxides, and this is most likely what actually happens. But in this case we always get as an impurity some of the sulfone, and we are unable to isolate a sufficiently pure sulfoxide by crystallization. It is quite likely that this is directly related to the recently established fact that mixed crystals may be formed of symmetrical sulfones and sulfoxides, [3].

We investigated the oxidation of sulfides of the following type:



in order to explore still further the oxidation reactions of various sulfides of the benzthiazole series.

These compounds were synthesized by condensing the potassium salt of mercaptobenzthiazole with chloroacetone, chloroacetic acid (and its ester), and ethylene chlorohydrin.

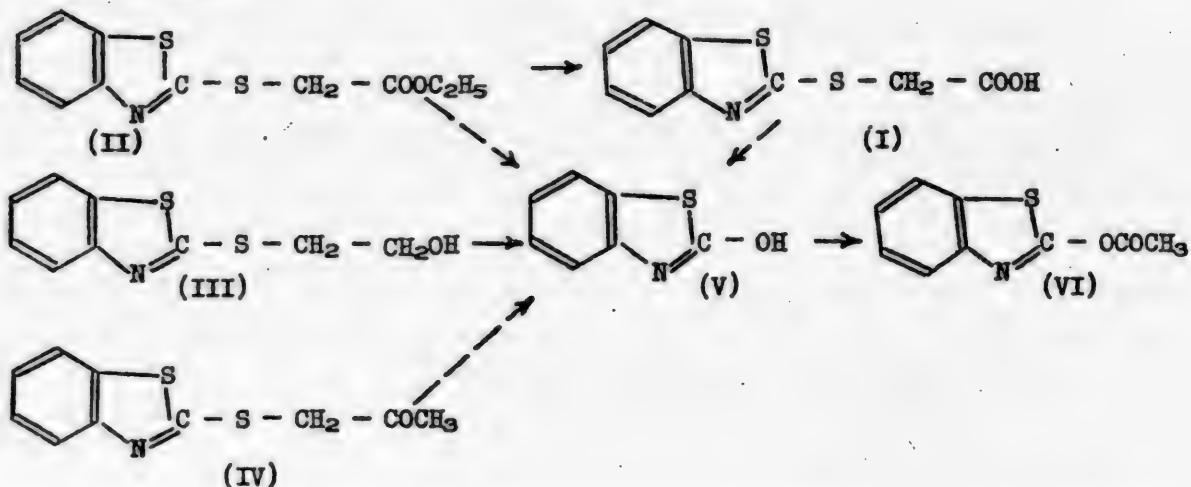
As has been established by our experiments, the oxidation of this type of compound is quite different from that of simple alkylbenzthiazolyl-2 sulfides, not yielding the corresponding sulfones. The mild action of H_2O_2 (1 mole) in acetic acid at room temperature does not cause the oxidation of sulfidic sulfur; after 3 to 4 days and after suitable treatment the initial compound is recovered with a greater or lesser admixture of tarry products of more complete oxidation. Oxidation by permanganate in weak alkaline solution results in deep-seated oxidative cleavage, after which it is impossible to isolate individual products. Only in oxidation with 2 moles of H_2O_2 in glacial acetic acid at 60-70° do we manage to secure an individual oxidation product. Under these conditions (cf. the experimental section below) benzthiazolyl-2-thioglycollic acid (I), its ethyl ester (II), benzthiazolyl-2-thioglycol (III), and mercaptobenzthiazolyl-2-acetone (IV) all yield the same substance upon oxidation: with a m.p. of 138-139°, a yield of 20-30%, which is found upon analysis to possess the general formula C_7H_5ONS .

This substance is readily soluble in alcohols and benzene and crystallizes from water or aqueous alcohol as colorless acicular crystals. It is readily soluble in aqueous solutions of alkalies, and upon acetylation with a mixture of acetic anhydride and acetic acid yields the acetate with a m.p. of 60-61°, which crystallizes from ethanol as colorless platelets and whose analysis satisfies the general formula $C_9H_7O_2NS$ (VI).

Analysis as well as the available literature data [4] suggest that the substance with a m.p. of 138-139° synthesized in the oxidation of sulfides of type C or D is the 2-hydroxybenzthiazole (V) described in the literature. As

was to be expected, both the substance and its acetate cause no depression of the melting point when mixed with pure 2-hydroxybenzthiazole and its acetate, respectively.

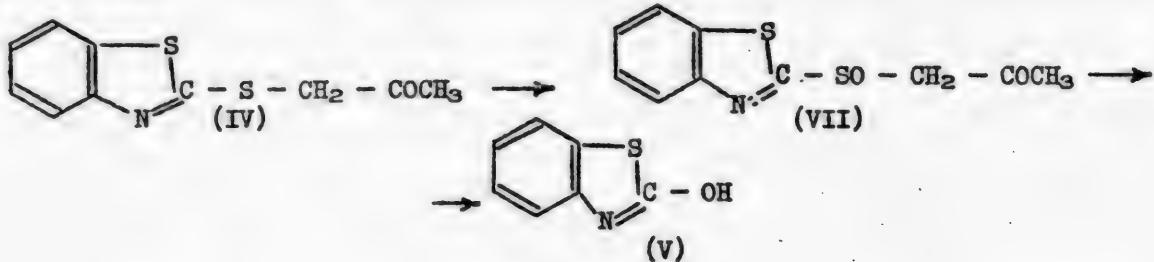
The oxidation of the products investigated may be represented by the following diagram:



Thus, the experimental data indicate that derivatives of mercaptobenzthiazole with these sulfidic groups: $-\text{S}-\text{CH}_2-\text{COR(C)}$ and $-\text{S}-\text{CH}_2-\text{CH}_2\text{OH}$ (D) suffer a rupture of the linkage between the sulfur and the carbon of the benzthiazole ring upon oxidation, resulting in the formation of 2-hydroxybenzthiazole.

It is as yet unclear in what degree this reaction proceeds in general via the intermediate formation of the sulfoxide. But when mercaptobenzthiazolyl-2-acetone (IV) is oxidized, we find that the oxidation products contain, in addition to 2-hydroxybenzthiazole (V), another substance with a m.p. of 117-118°, which is shown to have the formula of the sulfoxide $\text{C}_{10}\text{H}_8\text{O}_2\text{NS}_2$ (VII) by analysis and molecular-weight determination, and can be further oxidized to 2-hydroxybenzthiazole (V).

This justifies the assumption that the oxidation of mercaptobenzthiazolyl-2-acetone involves the intermediate formation of the corresponding sulfoxide, as follows:



In all other cases we were unable to isolate the corresponding sulfoxide.

EXPERIMENTAL

1. Synthesis of Alkylbenzthiazolyl Sulfides

1 mole of the corresponding alkyl halide is added to 1 mole of the potassium salt of mercaptobenzthiazole in 5 to 6 times the quantity of absolute alcohol, and the mixture is boiled for 3-4 hours over a water bath. Almost all the alcohol is boiled away, and 8 to 10 times the volume of water is added to the residue, which is then extracted with ether.. The ether layer is washed with water and desiccated over anhydrous potash, after which the ether is driven off and the residue distilled in a vacuum of 1-2 mm. The sulfides, which solidify upon cooling, are recrystallized from absolute alcohol. They are fairly soluble in most of the ordinary organic solvents. The constants and yields of some of the sulfides synthesized by us are listed in the table.

A certain amount of mercaptobenzthiazole that is insoluble in ether is always obtained when the alkylbenzthiazolyl sulfides are synthesized with alcohol that is not absolute.

2. Synthesis of Alkylbenzthiazolyl Sulfones

2 moles of 27% hydrogen peroxide are gradually added, with stirring, at 60° to a solution of 1 mole of the sulfide in 5-6 times the quantity of glacial acetic acid. After this has been done the reaction mass is heated for 3-4 hours, and then almost all the acetic acid is driven off in vacuum. A large amount of water is added to the residue, and the precipitate that forms is filtered out, washed with water, desiccated, and recrystallized from alcohol or acetone. The constants of some sulfones are listed in the accompanying table.

3. Synthesis of Ethyl Benzthiazolyl-2-thioglycollate (II)

14.7 g (0.12 mole) of ethyl chloroacetate is slowly added, with constant stirring and chilling, to a solution of 20 g (0.12 mole) of mercaptobenzthiazole in 300 ml of a 5% solution of Na_2CO_3 . The emulsion initially produced turns into a suspension upon stirring. After stirring for two hours at room temperature, the precipitate formed is filtered out, washed with water, and air dried. Weight: 24 g. M.p. 40-60° (not sharp). The precipitate is dissolved, with heating, in 200 ml of ligroin (b.p. 60-65°). The portion that is insoluble in ligroin is filtered out (weight 2.5 g); its m.p. is 176-178°, and it proves to be the initial mercaptobenzthiazole. The ligroin solution is evaporated in vacuum at 40-45°; the oily residue solidifies upon cooling. Double recrystallization from petroleum ether yields 16 g (52.8%) of colorless flat crystals with a m.p. of 42-44°.

0.1092 g substance: 5.6 ml N_2 (22°, 740 mm).

0.1018 g substance: 0.1900 g BaSO_4 .

Found %: N 5.62; S 25.63.

$\text{C}_{11}\text{H}_{11}\text{ONS}_2$. Calculated %: N 5.53; S 25.31.

4. Synthesis of Benzthiazolyl-2-thioglycollic Acid (I)

a) A solution of 2.9 g of chloroacetic acid in 40 ml of a 10% solution of Na_2CO_3 is added to a solution of 5 g of mercaptobenzthiazole in 50 ml of a 10% solution of Na_2SO_3 , and the mixture is heated for 2 hours over a water bath. Upon cooling, the transparent solution is acidified with concentrated HCl until it

* The analyses were performed in our laboratory by F. V. Rasina

reacts acid with Congo red; the precipitate formed is filtered out, carefully washed with water, and desiccated. Weight: 5.2 g; m.p. 150-153°. Double recrystallization from 70% methanol yields 4.1 g of colorless flat crystals with a m.p. of 153.5-154°. The product is hardly soluble in acetone and is insoluble in ligroin or benzene. Yield: 62.1%.

0.1106 g substance: 5.9 ml N₂ (20°, 753 mm).

0.1900 g substance: 0.3930 g BaSO₄.

Found %: N 6.00; S 28.44.

C₉H₇O₂NS₂. Calculated %: N 6.21; S 28.42.

b) 3 g of ethyl benzthiazolyl-2-thioglycollic acid is heated with 20 ml of a 10% solution of KOH until dissolution is complete. 40 ml of hot water is added to the solution, the hot solution is filtered with charcoal, and the filtrate is acidified with dilute HCl. The precipitate formed is filtered out, washed with water, and desiccated. This yields 2 g of a substance with a m.p. of 153-154° that causes no depression of the melting point when mixed with the substance synthesized by the previous method.

5. Synthesis of Benzthiazolyl-2-thioglycol (III)

16.5 g of ethylene chlorohydrin is added to a solution of 42 g of the potassium salt of mercaptobenzthiazole in 150 ml of absolute alcohol, and the mixture is heated for 3 hours over a water bath. When almost all the alcohol is driven off, 200 ml of water is added to the residue, and the mixture is extracted three times with 100 ml of ether each time. The ether /fractions are washed twice with a 10% solution of KOH, then carefully washed with water, and desiccated over anhydrous Na₂SO₄. Driving off the ether leaves behind a thick yellow oil that does not distill in vacuum at 1 mm; after 10 hours in a refrigerator it solidifies into a waxy yellow mass (35 g). The product is purified by dissolving it in boiling petroleum ether, from which it settles out upon cooling as a light-yellow oil that solidifies fairly rapidly; this treatment leaves a certain residue of dark tar that is insoluble in petroleum ether. Repeating this refining process yields 22 g of a light-yellow deposit with a m.p. of 45-48°. The product was twice recrystallized from a 2:1 mixture of ether and petroleum ether; this yielded 15 g of a substance with a constant m.p. of 57.5-58°. Yield: 34.7%.

0.1144 g substance: 6.8 ml N₂ (22.5°, 742.5 mm)

0.1446 g substance: 0.3182 g BaSO₄.

Found %: N 6.64; S 30.22.

C₉H₈ONS₂. Calculated %: N 6.63; S 30.35.

6. Synthesis of Mercaptobenzthiasolyl-2-acetone (IV)

17 g of chloroacetone is added, with chilling and stirring, to a solution of 30 g of mercaptobenzthiazole in an excess of a 5% solution of potash, after which the mixture is heated for 1 hour over a water bath. The oil that is formed solidifies upon cooling; it is filtered out, washed with water, and dried in air (26.5 g). The deposit is dissolved in hot methanol and filtered with charcoal; water is added to the filtrate until all the deposit formed precipitates out. This yields 22.5 g of slightly yellow acicular crystals with a m.p. of 65-67°.

Double recrystallization from 70% methanol yields colorless acicular crystals with a constant m.p. of 70-71°. Yield: 48.5%.

0.1134 g substance: 6.45 ml N₂ (19°, 759 mm).
0.1130 g substance: 6.30 ml N₂ (18°, 757 mm).
Found %: N 6.58, 6.46.
C10H9ONS2. Calculated %: N 6.27.

7. Oxidation of Benzthiazolyl-2-thioglycollic Acid

7 ml of 27% hydrogen peroxide (0.056 mole) is added drop by drop with constant stirring at 60° to a solution of 6 g (0.027 mole) of benzthiazolyl-2-glycollic acid in 60 ml of glacial acetic acid, after which the reaction product is heated for 1.5 hours over a water bath at 60-70°. Half of the acetic acid is driven off in vacuum, and the residue is poured into 100 ml of water. The precipitate that forms is filtered out, washed with water, and desiccated. Weight: 1.8 g; m.p. 125-130° (not sharp). Crystallization from a large amount of hot water or from a 2:1 alcohol-water mixture with activated charcoal added yields a colorless, finely crystalline precipitate with a m.p. of 138-139°.

0.1144 g substance: 9.35 ml N₂ (21°, 748 mm)
0.1468 g substance: 0.2216 g BaSO₄.
Found %: N 9.13; S 20.74.
C7H8ONS. Calculated %: N 9.26; S 21.20.

Analysis shows that this substance is 2-hydroxybenzthiazole (V). To confirm this, its acetate was synthesized: 3 g of the substance was dissolved in 20 ml of acetic anhydride, and the mixture was boiled with a reflux condenser for 1 hour. The acetic anhydride was driven off in vacuum, and 50 ml of water was added to the residue. The oil that separated out gradually solidified; the product was filtered out, washed with water, and air dried. Weight: 3.4 g; m.p. 57-58°. Recrystallization from ethyl alcohol yielded 2.8 g of flat crystals with a m.p. of 60-61°, which is the melting point of 2-hydroxybenzthiazole acetate.

0.1120 g substance: 7.65 ml N₂ (20°, 734 mm).
0.1354 g substance: 0.1616 g BaSO₄.
Found %: N 7.62; S 16.39.
C8H7O2NS. Calculated %: N 7.25; S 16.58.

8. Oxidation of Benzthiazolyl-2-thioglycol

5 ml of 27% hydrogen peroxide (0.04 mole) is added to a solution of 4.2 g (0.02 mole) of benzthiazolyl-2-thioglycol in 20 ml of acetone, and the mixture is heated over a water bath for 2 hours. The acetone is driven off, and 150 ml of water is added to the residue. The heavy yellow oil that settles out upon standing does not crystallize. It is separated from the aqueous layer, dissolved in hot 80% methanol, and filtered with charcoal. 1.1 g of pale yellow crystals separate out of the filtrate upon cooling; after double recrystallization from aqueous alcohol and charcoal they have a m.p. of 138-139° and cause no depression of the melting point when mixed with the 2-hydroxybenzthiazole synthesized by the oxidation of benzthiazolyl-2-thioglycolic acid.

9. Oxidation of Mercaptobenzthiazolyl-2-acetone

24 ml of 27% hydrogen peroxide (0.19 mole) is added at 60°, with constant stirring, during one hour to a solution of 20 g (0.09 mole) of mercaptobenzthiazolyl-2-acetone in 120 ml of glacial acetic acid. The homogeneous mixture is kept at 60° for 2 hours, after which the acetic acid is driven off in vacuum

until the volume is reduced to one-fourth. After the residue has been kept in a refrigerator overnight, a yellow crystalline deposit settles out; this is filtered out and washed with a small amount of ligroin. Weight: 2.5 g; m.p. 112-116° (not sharp).

Double recrystallization from methanol with charcoal yields 1.5 g of colorless acicular crystals with a m.p. of 117-118°.

3.775 mg substance: 2.00 ml N₂ (15°, 724 mm).

4.264 mg substance: 2.21 ml N₂ (15°, 774 mm)

Found %: N 5.98, 5.83.

C₁₀H₉O₂NS₂. Calculated %: N 5.85.

Found: M 235.2, 242.5 (Sol.)

C₁₀H₉O₂NS₂. Calculated: M 239.3.

The analysis and molecular weight of this product indicate that it has the formula of the sulfoxide (VII). Further oxidation of this product with hydrogen peroxide results in a product with a m.p. of 137-139°, which is identical with 2-hydroxybenzthiazole. After substance (VII) has been removed, the acetic-acid filtrate is diluted with three times its volume of water. The dark tarry substance that separates out is dissolved in a 10% solution of NaOH after the aqueous layer has been decanted; the alkaline solution is filtered with charcoal, and the filtrate acidified with 30% H₂SO₄ until it reacts acid with Congo red. The oil that separates out is extracted with ether, and the ether extract washed with water and desiccated over anhydrous Na₂SO₄. After the ether has been driven off, a yellow crystalline deposit settles out; it is filtered out, washed with benzene and dried. Weight: 3.6 g; m.p. 132-137° (not sharp). Double recrystallization from 2:1 aqueous alcohol and charcoal yields 2.1 g of colorless crystals with a m.p. of 137-139°, which cause no depression of the melting point when mixed with the 2-hydroxybenzthiazole synthesized in the previous oxidation reactions.

SUMMARY

1. A general method for oxidizing alkylbenzthiazolyl sulfides to the corresponding sulfones is described.

2. It is shown that mercaptobenzthiazole derivatives that contain the -S-CH₂-COR and -S-CH₂-CH₂OH sulfide groups yield 2-hydroxybenzthiazole when oxidized with hydrogen peroxide in glacial acetic acid.

3. It is shown, using mercaptobenzthiazolyl-2-acetone as an example, that the corresponding sulfoxide may be formed in the intermediate stage of oxidation to 2-hydroxybenzthiazole.

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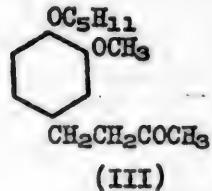
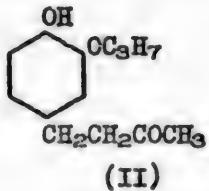
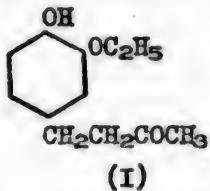
DERIVATIVES OF ZINGERONE. III

A. Y. Berlin, S. M. Sherlin(deceased), and T. A. Serebrennikova

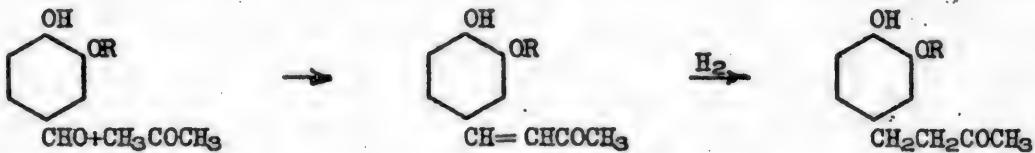
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In the course of our further study * of the relationship between the chemical structure and physiological activity of the aliphatic-aromatic ketones whose structures resemble that of zingerone, we synthesized a number of compounds characterized by: a) a change in the length of the alkoxyl radical; b) the presence of an amino group instead of phenolic hydroxyl in the aromatic ring; and c) a change in the position of the carbonyl group in the side chain.

Among the compounds belonging to the first of these groups we synthesized 4-hydroxy-3-ethoxyphenyl ethyl methyl ketone (I), 4-hydroxy-3-propoxymethyl ketone (II), and 4-isooamyloxy-3-methoxyphenyl ethyl methyl ketone (isooamylzingerone) (III):



The (I) and (II) homologues of zingerone were synthesized from the respective esters of protocatechuic aldehyde and acetone by the general method employed for the synthesis of zingerone and other substituted derivatives of benzylacetone:

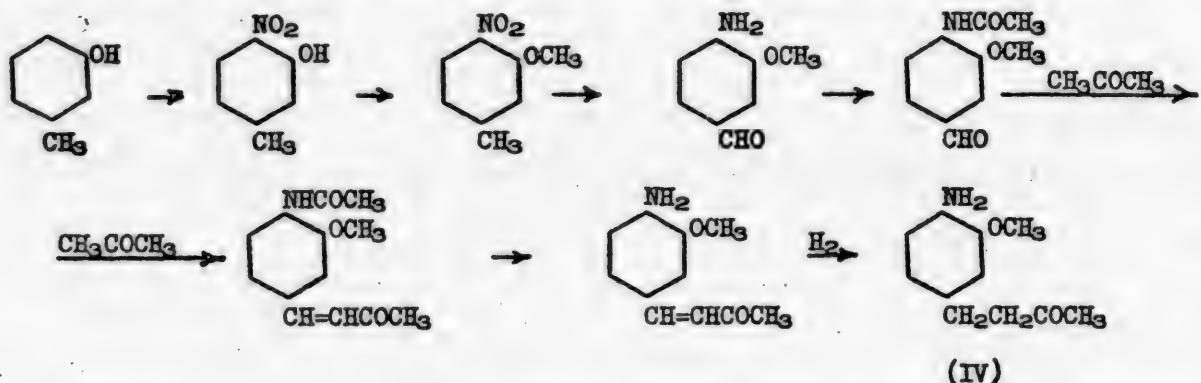


Isoamylzingerone (III) was synthesized by alkylating zingerone with isooamyl bromide [1].

Of the compounds of this type that contain an aromatic amino group, the amino analogues of zingerone and isozingerone were synthesized. 4-Amino-3-methoxyphenyl ethyl methyl ketone (IV) was synthesized as follows: the methyl ester of

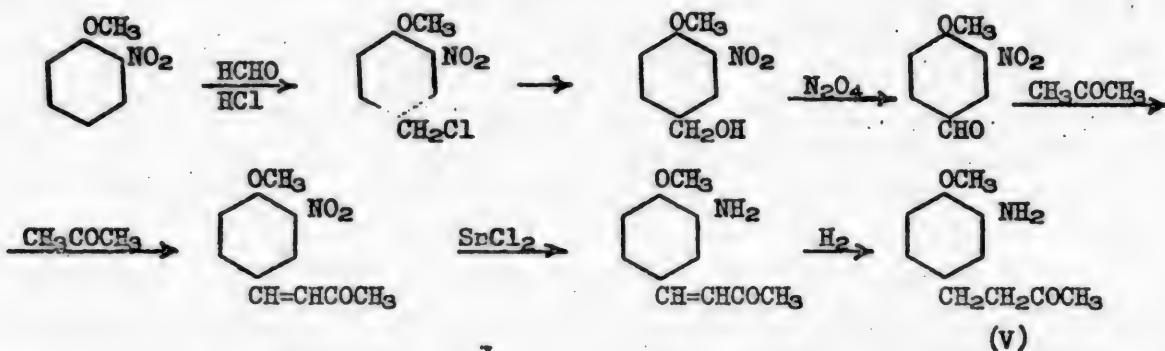
* Cf. our previous report.

4-nitro-m-cresol, prepared by the nitration of m-cresol and subsequent methylation [2] was converted by the action of sulfur into 4-amino-3-methoxy-benz-



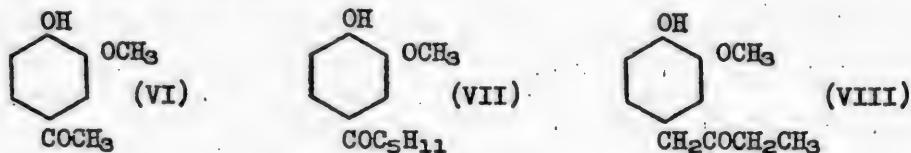
aldehyde [3]. Condensation of the acetyl derivative of this amine with acetone in an alkaline medium yielded the corresponding styryl ketone, which was then subjected to saponification and catalytic hydrogenation.

4-Methoxy-3-aminophenyl ethyl methyl ketone (V) was synthesized as follows:



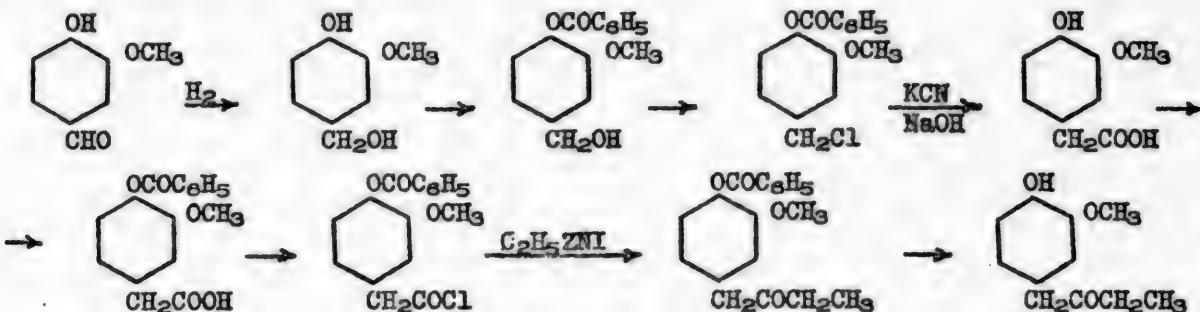
4-Methoxy-3-nitrobenzyl chloride [4] was synthesized from o-nitroanisole by the action of paraformaldehyde in the presence of hydrogen chloride; saponification and subsequent oxidation by nitrogen dioxide converted it into the corresponding aldehyde [5]. The synthesized methoxynitrobenzaldehyde was condensed with acetone [6], after which the nitro group was reduced and the double bond hydrogenated.

A substance of the zingerone type, but with a different position of the carbonyl group in the side chain, yielded 4-hydroxy-3-methoxyphenyl methyl ketone (acetovanillone) (VI) [7], 4-hydroxy-3-methoxyphenyl isoamyl ketone (VII), and 4-hydroxy-3-methoxybenzyl ethyl ketone (VIII):



The 4-hydroxy-3-methoxyphenyl alkyl ketones (VI) and (VII) are synthesized fairly easily from the corresponding esters of guaiacol by the Fries reaction.

To synthesize the 4-hydroxy-3-methoxybenzyl ethyl ketone, the benzoate of vanilllic alcohol was converted into the corresponding benzyl chloride by the action of thionyl chloride [8]:



from which we obtained homovanillic acid by the action of potassium cyanide, followed by saponification. Then the chloroanhydride of benzoylated homovanillic acid was converted by the action of ethylzinc iodide into a benzoyl derivative of the ketone, which was then subjected to saponification.

All the substances synthesized by us were subjected to a taste test; it was found that only one of these substances, namely, 4-hydroxy-3-methoxybenzyl ethyl ketone (VIII), produced a stinging sensation that was about as strong as that of zingerone. The other substances had almost no biting taste.

EXPERIMENTAL

4-Hydroxy-3-ethoxyphenyl Ethyl Methyl Ketone (I).

28 ml of a 10% solution of sodium hydroxide was added to a solution of 10 g of 4-hydroxy-3-ethoxybenzaldehyde in 40 ml of acetone, causing the mixture to turn light yellow. Four hours later the mixture was dark brown and had turned into a mass of long acicular crystals. Dilution with threefold the volume of water and acidulation with hydrochloric acid caused crystalline 4-hydroxy-3-ethoxystyryl methyl ketone to settle out as a light bulky precipitate. Recrystallization from dilute alcohol yielded the product in the form of pale yellow crystals with a m.p. of 102°. The yield was 12 g, i.e., quantitative.

3.250 mg substance: 8.338 mg CO₂; 1.926 mg H₂O.

Found %: C 69.97; H 6.63.

C₁₂H₁₄O₃. Calculated %: C 69.9; H 6.8.

The styryl ketone (12 g) thus synthesized was reduced in 300 ml of water, with vigorous stirring, by 150 g of 3% sodium amalgam. After the mercury had been removed and the solution acidulated, the product was extracted with ether, and the ether extract washed and desiccated with anhydrous sodium sulfate. Then the ether was driven off, and the product distilled in vacuum; it crystallized in the receiver. B.p. 182-183° at 13 mm; m.p. 34-35°.

3.561 mg substance: 9.007 mg CO₂; 2.471 mg H₂O.
Found %: C 68.98; H 7.76
C₁₂H₁₆O₃. Calculated %: C 69.2; H 7.7.

4-Hydroxy-3-propoxyphenyl Ethyl Methyl Ketone (II)

a) 4-Hydroxy-3-propoxybenzaldehyde. A mixture of 35 g of nitrobenzene and 100 g of 20% oleum was heated for 3 hours over an oil bath at 138-140°. Upon cooling, the mixture was poured into 3 liters of water, and the solution was filtered. To the yellow solution of nitrobenzosulfonic acid thus prepared there was added, with stirring, 27 g of mono-n-propyl ester of pyrocatechol (b.p. 97-99° at 8 mm [9]). The reaction mixture was immersed in a water bath at 28-30°, after which 20 g of formalin (about 30% formaldehyde) was added, and then 35 g of iron shavings were gradually added during the course of 2 hours, with continued stirring. The next day the product was extracted with ether, and the ether solution desiccated.

After the solvent had been driven off, the residue was subjected to fractionation in vacuum. This yielded 12 g of the unreacted monopropyl ester of pyrocatechol and 7 g of the hydroxypropoxybenzaldehyde with a b.p. of 163-165° at 13 mm. The synthesized product crystallized in the receiver and was twice recrystallized from benzene. Colorless crystals with a m.p. of 84°.

2.900 mg substance: 7.140 mg CO₂; 1.855 mg H₂O.
3.584 mg substance: 8.840 mg CO₂; 2.294 mg H₂O.
Found %: C 67.15, 67.25; H 7.16, 7.16.
C₁₀H₁₂O₃ Calculated %: C 66.7; H 6.67.

b) 4-Hydroxy-3-propoxystyryl methyl ketone. 25 ml of a 10% solution of sodium hydroxide was added to a solution of 9 g of 4-hydroxy-3-propoxybenzaldehyde in 35 ml of acetone. Five days later the dark yellow liquid was diluted with three times its own volume of water and acidified with hydrochloric acid until the Congo red reaction was acid. The yellow precipitate formed was separated out and recrystallized from alcohol. Yellow acicular crystals with a m.p. of 111°. The yield was 8.6 g.

2.808 mg substance: 7.288 mg CO₂; 1.858 mg H₂O.
3.338 mg substance: 8.618 mg CO₂; 2.200 mg H₂O.
Found %: C 70.20, 70.41; H 7.40, 7.37.
C₁₃H₁₆O₃. Calculated %: C 70.9; H 7.27.

c) 4-Hydroxy-3-propoxyphenyl ethyl methyl ketone. 110 g of 3% sodium amalgam was added in small portions during the course of 1.5 hours with vigorous stirring to a suspension of 8.6 g of styryl ketone in 220 ml of water. After reduction was complete, the mercury was separated out, and the alkaline solution was filtered and acidulated with hydrochloric acid. The product was extracted with ether, and the ether extract was desiccated with anhydrous sodium sulfate. After the ether had been driven off, the residue was distilled in vacuum, the substance crystallizing in the receiver as a colorless crystalline mass. B.p. 197-198° at 16 mm. M.p. 36-37°.

3.402 mg substance: 8.707 mg CO₂; 2.508 mg H₂O.
2.902 mg substance: 7.413 mg CO₂; 2.164 mg H₂O.
Found %: C 69.80, 69.67; H 8.25, 8.34.
C₁₃H₁₆O₃. Calculated %: C 70.3; H 8.11.

Isoamylzingerone (4-Isoamylhydroxy-3-methoxyphenyl ethyl methyl ketone) (III)

A mixture of 5 g of zingerone, 6 g of acetone, 3.7 g of powdered potash, and 4 g of isoamyl bromide was heated with a reflux condenser for 5 hours over a water bath. Then, after water had been added, the product was extracted with ether, and the ether extract washed with an alkali solution and then with water and desiccated with calcium chloride; the ether was driven off, and the crystalline residue recrystallized from petroleum ether. Colorless needles with a m.p. of 33-33.5°.

0.1077 g substance: 0.2844 g CO₂; 0.0876 g H₂O.
0.1089 g substance: 0.2879 g CO₂; 0.0906 g H₂O.
Found %: C 72.02, 72.08; H 9.10, 9.31.
C₁₆H₂₄O₃. Calculated %: C 72.73; H 9.09.

4-Amino-3-methoxyphenyl ethyl methyl ketone (IV)

In synthesizing 4-nitro-m-cresol [2] we found that the nitration of m-cresol is best effected in the temperature range -2° to +3°.

a) Methyl 4-nitro-m-cresylate. 60 ml of a 17% solution of sodium hydroxide, heated to 100°, was added in a single batch, with vigorous stirring, to a mixture of 30 g of the nitrocresol and 75 ml of water contained in a 500 ml three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser. Then 24 ml of dimethyl sulfate was added drop by drop to the mixture with continued stirring and heating over a boiling water bath, after which the mixture was heated for another 20 minutes. Then another 5 ml of dimethyl sulfate was added, and, after 10 minutes had elapsed, a solution of sodium hydroxide until litmus paper reacted alkaline. This alternate addition of dimethyl sulfate (5 ml at a time) and caustic alkali was continued (4 to 5 times) until the onset of an alkaline reaction caused the reaction mass to turn redder. After the end of the reaction another 25 ml of a 10% solution of sodium hydroxide was added to the mixture, which was then cooled, and the product extracted with ether. The ether solution was washed with a 2% alkaline solution and desiccated with calcined potash. After the ether had been driven off 27.6 g of the crystalline methyl ester was left. Single recrystallization from alcohol resulted in a m.p. of 58-59° (according to the literature [2] the m.p. is 62°).

b) 4-Amino-3-methoxybenzaldehyde. This was synthesized by the action of sulfur upon the methyl ester of 4-nitro-m-cresol, as described in the literature [3].

c) 4-Acetyl amino-3-methoxybenzaldehyde. A mixture of 2 g of aminomethoxybenzaldehyde, 10 g of acetic anhydride, and 3 g of anhydrous sodium acetate was heated to boiling for 30 minutes and poured into 100 ml of water after it had cooled. The oily product that separated out solidified after the acid solution had been neutralized with soda and then was recrystallized from benzene. M.p. 147° [3]. The yield was 1.8 g. The yield diminishes when large batches of the aminoaldehyde are acetylated.

d) 4-Acetyl amino-3-methoxystyryl methyl ketone. A solution of 3 g of the acetylaminomethoxybenzaldehyde in 30 ml of acetone was poured, with vigorous stirring, into 100 ml of water. 4 ml of a 40% solution of sodium hydroxide was added to the suspension that formed, after which the stirring was continued for

another 2 hours. The product was extracted with chloroform, and the extract washed with dilute hydrochloric acid and then with water, after which it was desiccated with anhydrous sodium sulfate. After the solvent had been driven off the crystallized residue was washed with benzene and dried. The yield was 3.5 g; m.p. 130-133°. After recrystallization from alcohol the product fused at 141-142°.

5.098 mg substance; 0.284 ml N₂ (25°, 750 mm)

Found %: N 6.16.

C₁₃H₁₅O₃N. Calculated %: N 6.01.

e) 4-Amino-3-methoxystyryl methyl ketone. A mixture of 1 g of the acetylaminomethoxystyryl methyl ketone and 20 ml of 20% sulfuric acid was heated over a boiling water bath until all the deposit had dissolved. The dark-yellow transparent solution that formed was extracted with ether, the aqueous solution alkalized, and the product extracted with chloroform. The extract was desiccated with anhydrous sodium sulfate, and the solution driven off. The slowly crystallizing residue was dissolved in benzene and cautiously precipitated with dilute petroleum ether; the first to settle out is a resin, followed by a yellow crystalline deposit with a m.p. of 99-102°. After recrystallization from a large quantity of water the saponification product was isolated as yellow needles with a m.p. of 102-103°. The yield was 0.202 g.

3.693 mg substance: 0.248 ml N₂ (31°, 754.5 mm).

Found %: N 7.27.

C₁₁H₁₃O₂N. Calculated %: N 7.33.

f) 4-Amino-3-methoxyphenyl ethyl methyl ketone. A solution of 1.8 g of the aminomethoxystyryl methyl ketone in 50 ml of alcohol is shaken up in an atmosphere of hydrogen in the presence of 0.1 g of platinum oxide. 260 ml of gas at 16° and 757 mm was absorbed in 15 minutes (computed absorption: 248 ml). The reaction mixture was poured into 200 ml of water, the product extracted with ether, and the ether extract desiccated with anhydrous sodium sulfate. After the ether had been driven off, the residue was fractionated in vacuum, a 177-179° fraction at 8 mm being collected. The product gradually crystallized upon standing, after which it was squeezed out on a porous dish and washed with petroleum ether. M.p. 40°.

4.205 mg substance: 0.272 ml N₂ (17.5°, 770 mm)

3.823 mg substance: 0.245 ml N₂ (17.5°, 770 mm).

Found %: N 7.61, 7.54.

C₁₁H₁₅O₂N. Calculated %: N 7.25.

The hydrochloride of the amine consists of yellowish crystals that melt at 182° with decomposition.

4-Methoxy-3-aminophenyl Ethyl Methyl Ketone (V)

a) 4-Methoxy-3-nitrobenzyl chloride was synthesized by passing hydrogen chloride through a mixture of o-nitro-anisole, paraformaldehyde, and gasoline [4].

b) 4-Methoxy-3-nitrobenzyl alcohol. A mixture of 34 g of methoxynitrobenzyl chloride, 630 ml of water, 25 g of potash, and 30 ml of alcohol was heated to boiling for 6 hours. The precipitate that settled upon cooling was drawn off, washed with water, and recrystallized from benzene. Yield: 23 g; m.p. 69-70°.

c) 4-Methoxy-3-nitrobenzaldehyde. A solution of 33.3 g of nitrogen

dioxide (8% excess), prepared from nitric acid, sp. gr. 1.4, and arsenic tri-oxide [10] was added to a solution of 61 g of the methoxynitrobenzyl alcohol in chloroform. The mixture soon grew cloudy and took on an emerald-green color. Five days later the solvent was driven off, and the residue recrystallized from alcohol. The yield of the aldehyde was 38 g, or 63% of theory. M.p. 80-82° [5].

d) 4-Methoxy-3-nitrostyryl methyl ketone. A mixture of 22 g of the methoxynitrobenzaldehyde, 200 ml of acetone, 700 ml of water, and 28 ml of a 40% solution of sodium hydroxide was stirred at room temperature for 5 hours. The precipitated yellow deposit was separated out and recrystallized from alcohol. The light-yellow crystals had a m.p. of 161-161.5°*. Yield: 21 g, i.e., 78% of theory.

e) 4-Methoxy-3-aminostyryl methyl ketone. 3 g of 4-methoxy-3-nitrostyryl methyl ketone was added in a single batch, with constant stirring, to a mixture, chilled to 5°, of 9.2 g of stannous chloride in 50 ml of concentrated hydrochloric acid, after which stirring was continued until the temperature of the reaction mass set in the freezing mixture was reduced to 2°. Half an hour later, the complex salt of the amine and the stannous chloride that separated out as a wine-red crystalline precipitate was filtered out, washed with concentrated hydrochloric acid, and air-dried. The salt was dissolved in as small a quantity of water as possible, and hydrogen sulfide was passed through the solution thus obtained until all the tin was precipitated. The precipitate of stannous sulfide was filtered out, the filtrate alkalized, and the methoxyamino-styryl methyl ketone that settled out was recrystallized from water. Light-yellow flat crystals with a m.p. of 128-128.5°. Yield: 1.2 g. The substance is readily soluble in dilute hydrochloric acid. Its solution in benzene or alcohol is unstable; tiny acicular crystals begin to settle out fairly soon. This phenomenon was not investigated any further.

4.473 mg substance: 0.411 ml CH₄ (0°, 760 mm)

Found %: (N) 0.412

C₁₁H₁₃O₂N. Calculated %: (N) 0.525

Determination of Molecular weight:

0.0921 g substance: 20.81 g benzene: Δt 0.12°.

0.0987 g substance: 20.87 g benzene; Δt 0.125°.

Found: 187.0; 191.4.

C₁₁H₁₃O₂N. Calculated: 191.0.

f) 4-Methoxy-3-aminophenyl ethyl methyl ketone. A solution of 0.9 g of the methoxyaminostyryl methyl ketone in 80 ml of alcohol was shaken in an atmosphere of hydrogen in the presence of 0.1 g of platinum oxide. The calculated quantity of gas was absorbed within half an hour, after which the solution was filtered and poured into 4 times its own quantity of water. The product was extracted with ether, and the ether solution desiccated with anhydrous sodium sulfate, after which the ether was driven off. The residue left after recrystallization from petroleum ether consisted of colorless acicular crystals with a m.p. of 56.5-57°. The substance is readily soluble in dilute hydrochloric acid.

3.216 mg substance: 8.104 mg CO₂; 2.201 mg H₂O.

2.720 mg substance: 6.862 mg CO₂; 1.873 mg H₂O.

4.838 mg substance: 0.328 ml N₂ (22°, 748 mm).

4.610 mg substance: 0.318 ml N₂ (23°, 747 mm).

Found %: C 68.72, 68.80; H 7.66, 7.70; N 7.58, 7.66

C₁₁H₁₅O₂N. Calculated %: C 68.39; H 7.77; N 7.25.

* Einhorn and Grabfield [6] cite the m.p. as 159°.

Acetovanillone (4-Hydroxy-3-methoxyacetophenone) (VI)

40 g of guaiacyl acetate was added to a chilled solution of 65 g of anhydrous aluminum chloride in 145 ml of anhydrous nitrobenzene. The mixture was heated to 80° for 45 minutes, after which it was allowed to stand for 24 hours at room temperature. The precipitated complex salt of the substance with aluminum chloride was drawn off without allowing moisture to get at it and then washed with benzene, then benzene and petroleum ether (mixed), and lastly with petroleum ether. After this treatment the product was a cream-colored crystalline powder. When the complex salt was carefully sprinkled into water that had been acidulated with hydrochloric acid, a white precipitate of acetovanillone was thrown down; it was separated out and recrystallized from water. M.p. 115-116°. Yield: 16 g.

4-Hydroxy-3-methoxy Phenyl Isoamyl Ketone (VIII)

The guaiacyl isocaproate, $\text{CH}_3\text{OC}_6\text{H}_4\text{OCOC}_5\text{H}_{11}$, was synthesized as follows: 14 g of isocapronyl chloride (prepared from the corresponding acid and thionyl chloride; m.p. 141-142°) was added drop by drop, with chilling, to a solution of 13.5 g of guaiacol in 70 g of pyridine. The next day the reaction mixture was diluted with water and acidulated. The oil that separated out was extracted with ether and dried with potash. B.p. 154° at 11 mm; 163° at 20 mm. A yellowish oily liquid. Yield: 15 g.

0.1113 g substance: 0.2873 g CO_2 ; 0.0806 g H_2O .

Found %: C 70.40; H 8.11.

$\text{C}_{13}\text{H}_{18}\text{O}_3$. Calculated %: C 70.27; H 8.11.

A solution of 33 g of anhydrous aluminum chloride in 150 ml of anhydrous nitrobenzene was mixed with 26.5 g of guaiacyl isocaproate. Soon after the mixing was complete the finely crystalline reaction product began to separate out. The reaction mixture was heated for 45 minutes at 80° over a water bath; it was observed that hydrogen chloride was evolved and the crystals dissolved. After 24 hours had elapsed, a crystalline precipitate settled out of the liquid; it was drawn off without allowing moisture to get at it and washed with benzene a benzene-petroleum ether mixture, and lastly with benzene again. The complex salt, a nearly white crystalline powder, was broken down by sprinkling it into water that was acidulated with hydrochloric acid. The oil that separated out, which did not crystallize even when deeply chilled, was extracted with ether, and the ether solution was dried with anhydrous sodium sulfate. Distillation yielded a thick, light-yellow oil that is soluble in alkalies. B.p. 205° at 21 mm. Yield: 10 g. The product crystallized upon standing; m.p. 35-36°.

0.1735 g substance: 0.4455 g CO_2 ; 0.1280 g H_2O .

Found %: C 70.03; H 8.25.

$\text{C}_{13}\text{H}_{18}\text{O}_3$. Calculated %: C 70.27; H 8.11.

4-Hydroxy-3-methoxybenzyl Ethyl Ketone (VIII)

a) Vanilllic alcohol was synthesized by the reduction of vanillin by hydrogen in the presence of platinum oxide [11]. Yield: 9.2%. M.p. 112°.

b) Benzoylvanilllic alcohol was synthesized by the benzoylation of vanilllic alcohol by the Schotten-Baumann reaction. It is advisable to perform this reaction in the presence of benzene as a solvent. The yield of the crude product was 90.5%. The m.p. was 96° after purification by dissolution in benzene and precipitation with petroleum ether.

c) 4-Benzoylhydroxy-3-methoxybenzyl chloride [8]. 0.5 g of calcium chloride was added to 20 g of thionyl chloride, after which 22 g of benzoylvanillic alcohol was added in small batches; the reaction mixture was then heated to 40-50° over a water bath for 15 minutes. Upon cooling, 50 ml of absolute alcohol was added to the crystallized mass; this dissolved a small quantity of the product together with colored impurities. The white, finely crystalline precipitate was filtered out and washed with cold ether. A small amount of the substance was also recovered from the ether mother liquor. Overall yield: 20.5 g. Recrystallization from alcohol yielded 17.5 g of the product as a white crystalline powder with a m.p. of 94°.

5.260 mg substance: 2.761 mg AgCl.

Found %: Cl 12.98.

$C_{15}H_{13}O_3Cl$. Calculated %: Cl 12.84.

d) Homovanillic acid. A mixture of 12 g of the benzoylhydroxymethoxybenzyl chloride, 8.5 g of potassium cyanide, and 50 ml of water was heated to boiling for 8-9 hours with a reflux condenser. Then 10 g of solid sodium hydroxide was added, and heating was continued until no more ammonia was liberated. The reaction mixture was diluted with water, filtered, and acidulated with hydrochloric acid until it gave an acid reaction with Congo red. The crystalline precipitate of benzoic acid that settled out was filtered out, and the mother liquor extracted with ether. After the ether had been driven off, the residue was treated with boiling cyclohexane. Upon cooling 0.5 g of homovanillic acid, with a m.p. of 137-139°, was precipitated from the cyclohexane. The product, which is insoluble in cyclohexane, was pressed on a porous dish and recrystallized from water. M.p. 138-141° [12]. Overall yield: 3.9 g.

e) Benzoylhomonillic acid, was synthesized by the benzoylation of homovanillic acid by the Schotten-Baumann reaction. The product was recrystallized first from ethyl acetate, and then from benzene with a small amount of ethyl acetate added. M.p. 169°. The yield was nearly quantitative.

2.969 mg substance: 7.302 mg CO_2 ; 1.360 mg H_2O .

Found %: C 67.06; H 5.12.

$C_{16}H_{14}O_5$. Calculated %: C 67.1; H 4.9.

The acid chloride was synthesized in the usual manner from the acid and thionyl chloride. It was recrystallized from petroleum ether. M.p. 66-67°; yield: 83.5%.

f) 4-Benzoylhydroxy-3-methoxy benzyl ethyl ketone. A solution of 7.9 g of benzoylhomonillic chloride in toluene was added drop by drop, with chilling by ice water and constant stirring, to a solution of ethylzinc iodide, prepared from 6.9 g of ethyl iodide and 5.7 g of zinc-copper fumes in the presence of 2.3 g of ethyl acetate and 4.6 g of toluene. After this process was completed the reaction mass was set aside to stand for half an hour at room temperature and then poured into water acidulated with dilute sulfuric acid, the resulting product being extracted with ether. The ether extract was washed with a solution of bicarbonate and hyposulfite, then with a dilute solution of ammonia, and dilute sulfuric acid, and, finally, dried with anhydrous sodium sulfate. After the solvent had been driven off, the residue was recrystallized from ice-chilled petroleum ether. Colorless crystals with a m.p. of 65-66.5°. Yield 5 g.

3.048 mg substance: 8.074 mg CO₂; 1.630 mg H₂O.
Found %: C 72.24; H 5.99.
C₁₈H₁₆O₄. Calculated %: C 72.48; H 6.04.

g) 4-Hydroxy-3-methoxybenzyl ethyl ketone. A mixture of 4.2 g of 4-benzoylhydroxy-3-methoxybenzyl ethyl ketone with a solution of 2.5 g of potassium hydroxide (80% KOH) in 50 ml of alcohol was heated with a reflux condenser over a water bath for 1.5 hours. The alcohol was driven off, and 50 ml of water was added to the residue, after which the unsaponified benzoyl derivative was extracted with ether. Carbon dioxide was passed through the aqueous solution until it was saturated, and the precipitated hydroxyketone was extracted with ether. After the ether extract had been desiccated with anhydrous sodium sulfate, the solvent was driven off, and the residue distilled in vacuum. A yellow liquid with a b.p. of 160-165° at 10-11 mm. Owing to the small quantity of product obtained (about 0.4 g) it was not feasible to refine it further.

3.858 mg substance; 9.464 mg CO₂; 2.474 mg H₂O.
3.005 mg substance: 9.354 mg CO₂; 2.474 mg H₂O.
Found %: C 66.90; 67.05; H 7.18, 7.23.
C₁₁H₁₄O₃. Calculated %: C 68.04; H 7.21.

Semicarbazone. A white crystalline powder. Purified by dissolution in chloroform and precipitation with petroleum ether. M.p. 154°.

3.105 mg substance: 0.463 ml N₂ (16°, 737 mm)
3.065 mg substance: 0.463 ml N₂ (20°, 737 mm)
Found %: N 17.08, 17.02.
C₁₂H₁₇O₃N₃. Calculated %: N 16.73.

SUMMARY

1. A number of compounds of the zingerone type have been synthesized, differing in the length of their alkoxy groups, the presence of an amino group instead of a phenolic hydroxyl group in the aromatic ring, and a change in the position of the carbonyl group in the side chain.

2. It was found that the approach of the carbonyl group to the aromatic ring in one link of the side chain does not weaken the biting taste of the series of compounds under investigation. Other changes in molecular structure result in complete or almost complete disappearance of activity.

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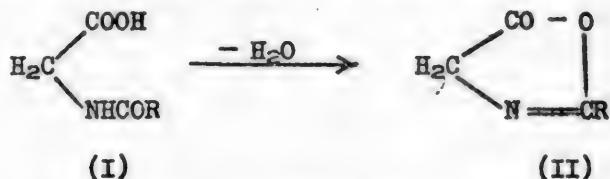
THE FORMATION OF OXAZOLONES FROM ACYL DERIVATIVES OF GLYCINE

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Beginning with the work of E. Erlenmeyer, Jr., as far back as 1892, an extremely large number of research papers has been devoted to the problem of the formation of oxazolones from alkylated alpha amino acids. It was established that it is best to effect this reaction at high temperature in the presence of acetic anhydride, and sometimes of sodium acetate as well (cf. also [1]), and it was found that under these conditions far from all the acylated alpha amino acids can be converted into oxazolones. At the present time it is held that this requires the substitution of various radicals for at least one, and preferably both of the hydrogen atoms attached to the alpha carbon atom of the molecule of the initial amino acid.

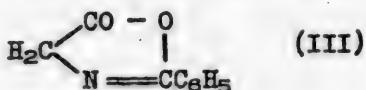
In fact, up to now there is no reference in the literature to the ability of hippuric acid and other acyl derivatives of glycine (I) to form the corresponding oxazolones of the general type (II) under the conditions specified above.



On the contrary, efforts made in this direction by E. Erlenmeyer [2] and by E. Mohr [3] in 1909-1910 led them to the conclusion that hippuric acid cannot possess this ability and that in the acyl derivatives of glycine the tendency to ring-closing as oxazolones can appear only after the attachment of substituents to the molecule's carbon atom that would facilitate the process of formation of the oxazolone ring. In 1940 this problem was again the subject of a theoretical study by A. E. Porai-Koshits and N. V. Khromov [4], who also reached the conclusion that the molecule of hippuric acid is not apt to possess the ability to be transformed into the corresponding oxazolone of type (II).

The theoretical considerations developed in the papers cited above did not seem to us to be sufficiently convincing, however, and as we saw it, the absence of substituents at the alpha carbon atom of acyl derivatives of glycine could not deprive them of the ability to be converted into oxazolones under the conditions that are usually fully satisfactory for acylated alpha amino

acids containing various radicals attached to the alpha carbon atom. That is why we thought it necessary to subject this problem to experimental investigation anew, first of all checking the experiments of E. Erlenmeyer and E. Mohr on hippuric acid, which yield only negative results, according to them. Another known foundation for this research of ours was the work of P. Karrer, who asserted that the oxazolone corresponding to hippuric acid may exist, although it is extremely unstable toward hydrolyzing substances. This oxazolone was synthesized by P. Karrer and R. Widmer as long ago as 1925 (unexpectedly for both of the authors) as the result of the action of diazomethane in an ether solution upon hippuryl chloride [5]. At first, these research workers ascribed the wrong structural formula to the compound they had isolated. But in 1941 this wrong formula was corrected by P. Karrer and G. Bussmann [6], who proved that the compound formed under these conditions is 2-phenyloxazolone-5 (III).



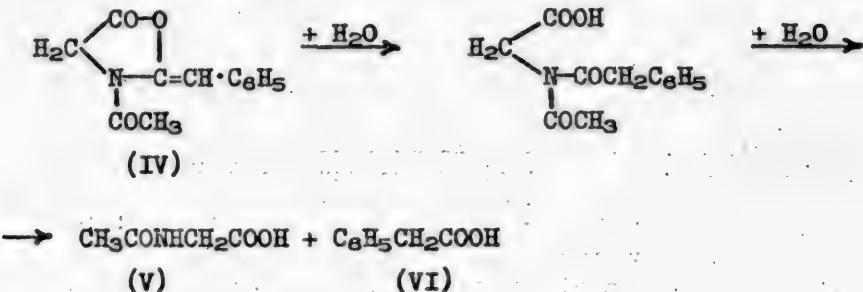
Inasmuch as the oxazolone (III) proved to be actually existent, even though it had been synthesized indirectly from hippuryl chloride, we felt that all the earlier assertions concerning the inability of hippuric acid itself to undergo the conversion into this oxazolone (III) under ordinary conditions were due to the false experimental observations of E. Erlenmeyer and E. Mohr. All these considerations compelled us to undertake the experimental study of the problem involving the ability of the acyl derivatives of glycine (I) to undergo conversion into oxazolones of type (II).

The first objects of our investigation were hippuric and phenaceturic acids. The reaction conditions chosen were those ordinarily recommended for the synthesis of the oxazolones of the acyl derivatives of alpha amino acids containing various substituents at the alpha carbon atom. As we had assumed, both hippuric and phenaceturic acids proved to be easily convertible into the respective oxazolones of type (II) under these conditions, and hence, this property is typical of the acyl derivatives of alpha aminocarboxylic acids in general, and not merely for those acids that contain one substituent or another at the alpha carbon atom.

We must deal briefly with the conditions for the formation of oxazolones of type (II) and with their properties. According to our data, hippuric acid is converted into 2-phenyloxazolone-5 (III) by prolonged heating with acetic anhydride. This oxazolone is a crystalline substance with a m.p. of 88-89°, which gradually turns into hippuric acid when exposed to air. This conversion takes place extremely quickly under the action of aqueous solutions of alkalies; that is why the isolation and purification of the oxazolone (III) requires suitable precautions. All the properties of the compound synthesized by us agree with those of the 2-phenyloxazolone-5 described by P. Karrer, for which he, however, cites a m.p. of 91° [5,6].

Like hippuric acid, phenaceturic acid can also be converted into the corresponding oxazolone of type (II) by heating with acetic anhydride. It is preferable, however, not to isolate this oxazolone as such, but as the N-acetyl derivative (IV), which can be readily synthesized by heating phenaceturic acid with acetic anhydride in the presence of anhydrous sodium acetate. This substance has the composition formula $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$ and is a white crystalline compound that fuses at 176-177°. When boiled with a 10% solution of sodium

hydroxide, it is completely cleaved, both phenylacetic acid and acetic acid being found among the decomposition products. The presence of an acetyl group attached to the nitrogen atom is due to the fact that when the substance is boiled with water, it breaks down into acetylglycine (V) and phenylacetic acid (VI). This is indubitable proof of the fact that the compound we isolated is actually 2-benzylidene-3-acetyloxazolone-5 (IV), whose cleavage into acetylglycine and phenylacetic acid can be represented as follows:



EXPERIMENTAL

1. Synthesis of 2-Phenylloxazolone-5

5 g of hippuric acid and 40 ml of acetic anhydride are heated for 20-25 minutes over a boiling water bath with intermittent stirring. Toward the end of the heating period the reaction mixture turns yellow, and sometimes orange. The solution produced is poured into a mixture consisting of 100 ml of ice water and 100 ml of benzene. The benzene layer is removed and washed a few times with a 1% solution of sodium bicarbonate and then with water. Then the benzene solution is desiccated for half an hour with sodium sulfate, and calcined potash is added to it. The latter is filtered out 15-20 minutes later, and the benzene solution is again desiccated with sodium sulfate. The dried benzene solution is usually red. The benzene is driven off in vacuum at a temperature no higher than 40°. The driving off of the benzene is stopped as soon as the cooled residue in the flask begins to crystallize. The crystalline mass is pressed on a porous plate and twice recrystallized from a very small quantity of absolute benzene. This yields acicular crystals with a m.p. of 88-89°, often light pink or cream-colored. The yield is usually 30-40%.

2-Phenylloxazolone-5 is readily soluble in ether, alcohol, chloroform, benzene, acetone, and ethyl acetate, and is nearly insoluble in petroleum ether or ligroin. When kept exposed to the air, it is gradually transformed into hippuric acid. When recrystallized from solvents containing traces of moisture, hippuric acid may be obtained instead of the oxazolone. This transformation occurs most readily when the oxazolone is treated with an aqueous solution of an alkali.

Found %: C 67.14; H 3.85; N 8.82.
 $C_9H_7O_2N$. Calculated %: C 67.08; H 4.34; N 8.69.

2. Synthesis of 2-Benzyliden-3-acetyloxazolone-5 (IV)

5 g of phenaceturic acid, 2.5 g of anhydrous sodium acetate, and 42 ml of acetic anhydride are heated, with efficient stirring, for 5 hours to 60-70°.

After heating is over, the reaction mixture, which consists of a white precipitate and an orange-red solution, is poured into 200 ml of ice water. A light-yellow oil separates out, which gradually crystallizes. The precipitate is filtered out and washed, at first with water a few times and then with ether. The yield is usually 35-40%. The substance is poorly soluble in water, chloroform, and ether. After recrystallization from ethyl alcohol or benzene its m.p. is 176-177°.

Found %: C 66.36; H 5.04; N 6.53.
 $C_{12}H_{11}O_3N$. Calculated %: C 66.35; H 5.06; N 6.45.

3. Properties of 2-Benzyliden-3-acetyloxazolone-5

a) Cleavage by an alkaline solution 6.5 g of the oxazolone (IV) is heated with 50 ml of a 10% aqueous solution of sodium hydroxide for 6 hours. The solution that forms is filtered and evaporated in vacuum to dryness. The dry residue is boiled for 5 hours with 20 ml of absolute ethyl alcohol in the presence of 1 ml of sulfuric acid. The reaction mixture is poured into water, neutralized with sodium bicarbonate, and extracted with ether. The ether extract is desiccated with sodium sulfate, and the ether is then driven off. The residue is fractionated with a good dephlegmator. At 60-80° a fraction is distilled that consists largely of ethyl acetate. The temperature is then quickly raised, and the subsequent fraction, which is ethyl phenylacetate, is distilled at 222-227°. Weight of this fraction: 2.4 g. The first fraction is boiled with a 20% aqueous solution of sodium hydroxide for 3 hours, after which the calculated quantity of an alcoholic solution of p-nitrobenzyl bromide is added to the solution, and heating is continued for another hour. The precipitate that settles out upon cooling is twice recrystallized from methanol. M.p. 78°. A mixture of this substance with p-nitrobenzyl acetate fuses at the same temperature.

The second fraction, which boils at 222-227°, is also saponified by heating with a 20% aqueous solution of sodium hydroxide for 3 hours. When the solution thus obtained is acidulated with 15% hydrochloric acid, shiny white crystals that fuse at 76° and cause no depression of the melting point when mixed with phenylacetic acid are precipitated.

b) Cleavage by water. 0.5 g of the oxazolone (IV) is boiled for 4 hours with 20 ml of water. The solution of the oxazolone is complete after 1 hour has elapsed. The solution is evaporated in vacuum to dryness, and the dry residue is repeatedly extracted with ether. After the ether has been driven off, 0.25 g of phenylacetic acid is left behind as white crystals that fuse at 72-74°. After recrystallization from water, it is converted into the p-nitrobenzyl ester, which fuses at 64-65°.

Found %: C 66.21; H 4.77.
 $C_{15}H_{13}O_4N$. Calculated %: C 66.42; H 4.80.

The dry residue, freed from the phenylacetic acid by repeated extraction with ether, is recrystallized from methanol. It is advisable to add ether to the alcohol solution to obtain complete precipitation of the substance. The precipitate is filtered out and washed with ether. This yields white crystals that fuse at 203° and cause no depression of the melting point when mixed with acetyl glycine.

Found %: C 41.37; H 5.54.
 $C_4H_7O_3N$. Calculated %: C 41.02; H 5.98.

SUMMARY

It has been shown that acyl derivatives of glycine (hippuric and phenaceturic acids) can be converted into the corresponding oxazolones. In the case of phenaceturic acid, it is preferable to isolate the oxazolone as the N-acetyl derivative.

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THE SYNTHESIS OF 4-CHLORO- AND 4-BROMO-1-AMINOANTHRAQUINONE AND OF THEIR BENZOYL DERIVATIVES BY THE SANDMEYER REACTION

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The 1-amino-4-chloro- and 1-amino-4-bromoanthraquinones, as well as their benzoyl derivatives, are compounds that are known in the literature. 1-Amino-4-chloroanthraquinone can be synthesized by one of the following methods: 1) the reduction of 4-chloro-1-nitroanthraquinone [1]; 2) the chlorination of 1-acetaminoanthraquinone, followed by splitting off the acetyl group [2]; 3) saponifying 2-chloro-4-benzoylaminoanthraquinone with concentrated sulfuric acid [3]; 4) treating 1,4-dichloroanthraquinone with aryl sulfonamides, followed by splitting off the acid group in sulfuric acid [4]; 5) halogenating 1-aminoanthraquinone in nitrobenzene in the presence of AlCl_3 and FeCl_3 [5].

The following methods are available for synthesizing 1-amino-4-bromoanthraquinone: 1) nitrating and reducing bromoanthraquinone [6]; and 2) removing the sulfo group from 1-amino-4-bromo-2-anthraquinonesulfonic acid under various conditions [7].

The benzoyl derivatives of 1-amino-4-chloro- and 1-amino-4-bromoanthraquinone can be prepared from 1-benzoylaminoanthraquinone by treating it with halogenating agents in various organic solvents, [8].

The present report describes a method of synthesizing the 1-amino-4-chloro- and 1-amino-4-bromoanthraquinones, as well as their benzoylation products, from 1-amino-4-benzoylaminoanthraquinone in a chemically pure state, with chlorine or bromine replacing the amino group (by the Sandmeyer reaction).

The advantage of this latter method resides in the fact that the introduction of the halogen into the anthraquinone group by means of the diazo reaction guarantees against the formation of side products and ensures the purity of the amino halogen anthraquinones.

The synthesis conditions were very much like those described in Goldstein's paper [9] for the synthesis of 1-anthraquinone iodide. It was found during the course of our investigation that the 1-benzoylamino-4-haloanthraquinones are much harder to purify than the 1-amino-4-haloanthraquinones; hence, the synthesized 1-benzoylamino-4-haloanthraquinones were first saponified by heating them with concentrated sulfuric acid.

The most effective method of purification proved to be the conversion of

the 1-amino-4-chloro- and 1-amino-4-bromoanthraquinones into the sulfates, after which the free base was separated out. This was repeated 4 to 5 times, after which we got chemically pure preparations. The benzoyl derivatives were synthesized by heating the chemically pure 1-amino-4-chloro- and 1-amino-4-bromoanthraquinones with benzoyl chloride in chlorobenzene.

Inasmuch as the principal goal of the present research was the synthesis of chemically pure preparations, it is quite possible that the data herewith published on the product yields may be improved by subsequent experimentation.

The research was done under the guidance of A.M.Lukin, for whose valuable counsel and advice the author is grateful.

1. Diazotization of 1-benzoylamino-4-aminoanthraquinone. 10 ml of sulfuric acid (sp. gr. 1.84) is poured into a porcelain cup and 3.42 (0.01 mole) of 1-benzoylamino-4-aminoanthraquinone is added in small batches, with constant stirring.

It usually takes an hour and a half at 20° for solution to be complete. Then 0.75 g of sodium nitrite is gradually added, the temperature being kept the same. The mixture is kept at 20° for two hours with constant stirring. The diazo solution is poured into a mixture of 400 g of ice and 200 ml of water and stirred for half an hour.

2. Substitution of chlorine or bromine for the diazo group. The 1-benzoylamino-4-diazoanthraquinone sulfate formed settles out as a light brown deposit, which is filtered in a Buchner funnel through a cotton-cloth filter. The filtrate contains the basic acid and a small amount of the diazonium compound. When a solution of cuprous chloride or anhydrous potassium bromide is added to the filtrate, a small amount of the 1-benzoamino-4-haloanthraquinone settles out; this is usually not recovered.

The diazonium precipitate on the filter is again treated a few times with ice water. If it is not too acid, the diazonium compound is soluble in water. As a rule the precipitate had to be treated with 1700-2000 ml of water to obtain complete dissolution. The dissolution of the diazonium compound should be done as quickly as possible, in an endeavor to prevent its decomposition. After dissolution is complete, either a solution of cuprous chloride (8 g of CuSO₄, 12 g of NaCl, and 40 ml of H₂O) prepared by Guben's method [10] or 4.8 g of potassium bromide is added to the solution. An acicular (under the microscope) precipitate is thrown down at once: this precipitate is brown in the case of 1-benzoylamino-4-bromoanthraquinone. The reaction mass is set aside to stand overnight, and the next morning it is heated for 30 minutes over a water bath, after which 20 ml of sodium bisulfite is added. Then the precipitated 1-benzoylamino-4-haloanthraquinone is filtered out and washed thoroughly on the filter with water. The weight of the dried precipitate averaged 1.88 g for 1-benzoylamino-4-chloroanthraquinone, or 52% of the theoretically computed value. The weight of the dry 1-benzoyl-4-bromoanthraquinone averaged 2 g, or 49.2% of the theoretical value.

3. Saponification of the benzoyl group. All the synthesized 1-benzoyl-amino-4-haloanthraquinone is heated to 90-100° with sulfuric acid, sp. gr. 1.84, in a porcelain cup over a water bath. The quantity of acid used is four times the weight of the 1-benzoylamino-4-haloanthraquinone. The heating is continued for 20-30 minutes with constant stirring. The reaction mass is poured into water after it has cooled. The precipitated amine is filtered

out, washed thoroughly with water to remove the acid, and dried at a temperature of no more than 100°. The weight of the dried 1-amino-4-chloroanthraquinone averaged 1.31 g, or 51.0% of the theoretical value, based on the initial 1-benzoylamino-4-aminoanthraquinone. The weight of the dried 1-amino-4-bromoanthraquinone averaged 1.38 g, or 45.8% of the theoretical value, based on the initial 1-benzoylamino-4-aminoanthraquinone.

4. Purification of the synthesized 1-amino-4-haloanthraquinones. All the synthesized product is dissolved in twice its volume of concentrated sulfuric acid, sp. gr. 1.84, and the sulfate is isolated by diluting the solution with water. The dilution is down to 70% concentration of sulfuric acid for 1-amino-4-chloroanthraquinone, and down to 65% concentration for 1-amino-4-bromoanthraquinone. After being kept at 0° for 2-3 hours, the sulfate is filtered out on a Schott funnel with a glass filter and washed with 50% sulfuric acid until the filtrate is almost colorless. Then the sulfate is decomposed with hot water and the free base is filtered out. This whole refining operation is repeated 3 to 5 times until the end product has a constant melting point. Finally, the synthesized 1-amino-4-haloanthraquinone is recrystallized from 60% acetic acid. The melting point remains constant. This refining yields 1-amino-4-chloroanthraquinone with a m.p. of 177.0-178.0° and a yield of about 70% of the substance to be refined.

6.420 mg substance: 3.57 mg AgCl.
7.563 mg substance: 4.131 mg AgCl.
4.472 mg substance: 0.213 ml N₂ (22°, 758 mm).
4.500 mg substance: 0.210 ml N₂ (22°, 758 mm).
Found %: Cl 13.76, 13.51; N 5.50, 5.39
C₁₄H₈O₂NCl. Calculated %: Cl 13.76; N 5.43.

1-Amino-4-bromoanthraquinone has a m.p. of 177.5-178.5°. The yield is about 65%, based on the amount of substance to be refined.

6.103 mg substance: 3.777 mg AgBr.
7.212 mg substance: 4.429 mg AgBr.
4.879 mg substance: 0.200 ml N₂ (22°, 749 mm).
6.742 mg substance: 0.272 ml N₂ (20°, 758 mm).
8.93 mg substance: 18.24 mg CO₂; 1.96 mg H₂O.
7.92 mg substance: 14.78 mg CO₂; 1.77 mg H₂O.
Found %: C 55.70, 55.83; H 2.46, 2.74; Br 26.33, 26.13;
N 4.67, 4.69.
C₁₄H₈O₂NBr. Calculated %: C 55.69; H 2.63; Br 26.45; N 4.63.

5. Benzoylation of 1-amino-4-haloanthraquinones. 4 g of the amino-4-chloro- or bromoanthraquinone is dissolved in 15-16 ml of chlorobenzene, and 8 ml of benzoyl chloride is added. Boiling is continued for 10 minutes. Upon cooling golden-yellow platelets of 1-benzoylamino-4-chloroanthraquinone or yellow needles of 1-benzoylamino-4-bromoanthraquinone settle out. The yield is about 90% of the theoretical value. The synthesized 1-benzoylamino-4-chloroanthraquinone has a m.p. of 237.5-238.5°.

3.990, 5.182 mg substance: 1.520, 2.020 mg AgCl.
4.140 mg substance: 0.144 ml N₂ (20°, 759 mm).
2.647 mg substance: 0.094 ml N₂ (23.5°, 753 mm).
Found %: Cl 9.43, 9.64; N 4.05, 4.05.
C₂₁H₁₂O₃NCl. Calculated %: Cl 9.80. N 3.87.

The synthesized 1-benzoylamino-4-bromoanthraquinone has a m.p. of 230-231°.

5.550 mg substance: 2.560 mg AgBr.
4.432 mg substance: 2.020 mg AgBr.
4.860 mg substance: 0.146 ml N₂ (22°, 761 mm).
3.519 mg substance: 0.107 ml N₂ (22.5°, 760 mm).

Found %: Br 19.80, 19.40; N 3.49, 3.51.

C₂₁H₁₂O₃NBr. Calculated %: Br 19.66; N 3.44.

SUMMARY

1-Amino-4-chloro- and 1-amino-4-bromoanthraquinone, as well as their benzoylation products, have been synthesized from 1-amino-4-benzoylaminoanthraquinone by replacing the amino group by chlorine or bromine in a Sandmeyer reaction.

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SYNTHESIS OF 2,3-DIBROMOFURAN AND THE STRUCTURE OF 3-BRomo- AND 3,5-DIBROMOPYROMUCIC ACIDS

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In measuring the dipole moments of mono- and disubstituted furans, we tried to synthesize dibromofuran, which is not described in the literature, by decarboxylating 3,5-dibromopyromucic acid, the structure of which had been established by Hill and Sanger [1]. We succeeded in effecting the decarboxylation and in isolating the corresponding dibromofuran in a pure state. We measured its dipole moment in a benzene solution, getting a value of 1.53 D, whereas the vector sum computed for 3,5-dibromofuran from the value of the moment for the C—Br bond taken from aliphatic compounds (2D) is only 0.76 D. Moreover, we found that the other halofurans have dipole moments that are much lower than those computed from the vector sums. The high value of the moment made us doubt whether the structure of 3,5-dibromopyromucic acid was correct.

In their paper on "Bromopyromucic Acids" [1], Hill and Sanger, who were the first to synthesize 3,5-dibromopyromucic acid, established its structure as well as the structure of the 3,4-dibromopyromucic acid that is isomeric with it and of the two isomeric monobromopyromucic acids on the basis of the products synthesized by the oxidation of these acids with dilute nitric acid, namely:

- 1) In the oxidation of the bromopyromucic acid with a m.p. of 183-184°, maleic acid is one of the products;
- 2) In the oxidation of the bromopyromucic acid with a m.p. of 128-129°, monobromofumaric acid is synthesized;
- 3) In the oxidation of the dibromopyromucic acid with a m.p. of 191-192°, dibromomaleic acid is synthesized;
- 4) In the oxidation of the dibromopyromucic acid with a m.p. of 167-168°, monobromofumaric acid is synthesized.

Besides, both of the dibromopyromucic acids are synthesized in the decomposition of pyromucyl tetrabromide by an alkali, whereas the monobromopyromucic acid with a m.p. of 128-129° can be synthesized from both dibromopyromucic acids by reducing them with zinc dust.

These facts led Hill and Sanger to the following conclusions:

- 1) The monobromopyromucic acid with a m.p. of 183-184° is 5-bromo-pyromucic acid;
- 2) The dibromopyromucic acid with a m.p. of 191-192° is 3,4-dibromo-pyromucic acid;
- 3) The dibromopyromucic acid with a m.p. of 167-168° is 3,5-dibromo-pyromucic acid;
- 4) The monobromopyromucic acid with a m.p. of 128-129°, synthesized from both the 3,4- and the 3,5-dibromopyromucic acids, is 3-bromopyromucic acid.

Moreover, in the reaction in which 3,5-dibromopyromucic acid is formed by the direct action of bromine upon pyromucic acid, it is apparent that the first bromine atom is first attached at position 5, since 5-bromopyromucic acid was isolated as one of the end products. This is also corroborated by all the experimental data without exception, which indicate that if there is a free alpha position, it is that position, and not the beta position, that is substituted. The orienting effect of the groups at the alpha position in the furan ring is the same as in the benzene ring, as was evident in a series of investigations. Hence, in 5-bromopyromucic acid position 4 is under the simultaneous orienting influence of the bromine (ortho orientation) and the carboxyl (meta orientation).

The direct action of bromine on the pyromucic acid should lead us to expect that 4,5-dibromopyromucic acid ought to be synthesized instead of 3,5-dibromopyromucic acid, as Hill and Sanger believed. This course of the reaction is corroborated just as when the sulfonation of 5-bromopyromucic acid yields the 4-sulfo acid.

The proof of the structure of α,β -dibromopyromucic acid given by Hill on the basis of the products obtained in its oxidation is not unequivocal, since the oxidation of 4,5-dibromopyromucic acid yields the same monobromo-maleic acid as in the oxidation of the 3,5-dibromopyromucic acid.

Gilman [2] also points out the undefined nature of the proof of the structure of 3,5-dibromopyromucic acid given by Hill.

It should be pointed out that the vector sum of the moments of the bonds for dibromofuran, corresponding to 4,5-dibromopyromucic acid, is 1.83 D (computed from the value of the moments of the following bonds: $C_{\alpha}-Br = 1.07$ D and $C_{\beta}-Br = 1.37$ D, based on the moments of α - and β -bromofurans).

Thus we can reach the following conclusions on the basis of the method of synthesizing α,β -dibromopyromucic acid and on the basis of the dipole moments of the dibromofuran, synthesized from this acid:

- 1) The bromine atoms in Hill's dibromopyromucic acid occupy positions 4 and 5, and not 3 and 5, as Hill assumed;
- 2) The dibromofuran synthesized by the decarboxylation of this acid is 2,3-dibromofuran; and
- 3) Hill's β -bromopyromucic acid, synthesized from the 3,4- as well as from the α,β -dibromopyromucic acid, is actually not the 3-bromo- but the 4-bromopyromucic acid.

EXPERIMENTAL

1. Synthesis of 4,5-dibromopyromucic acid. 4,5-dibromopyromucic acid was synthesized by us according to the Hill and Sanger method [1]: the bromination of pyromucic acid without a solvent. The bromination product was twice crystallized from water and converted into the barium salt; after separation from the salt the dibromopyromucic acid was recrystallized from water. M.p. 170.5-.71.2°. The melting point did not change after a check crystallization from water. The melting point remained the same after another treatment with barium chloride and recrystallization of the isolated free acid. Hill and Sanger give the m.p. as 167-168°.

2. Synthesis of 2,3-dibromofuran. 2,3-Dibromofuran was synthesized by decarboxylating 4,5-dibromopyromucic acid in quinoline. The decarboxylation apparatus consisted of a short-necked round-bottomed flask, sealed with a stopper, through which there passed a fractionating column, a thermometer, and a tube with a drawn-out tip for passing gas through. The fractionating column was fitted with a thermometer and connected to a large condenser. The receiver, hermetically joined to the condenser, was, in turn, connected to a trap fitted with an ogee. The ogee served to check the flow of gas. Behind the ogee there was a Bunsen flask connected through a three-way stopcock to a water-jet pump.

For decarboxylation we took 2 g of 4,5-dibromopyromucic acid, 20 g of quinoline, and 1 g of copper powder (Naturkupfer C). Before heating was commenced, the whole apparatus was filled with illuminating gas, dried by passing it through sulfuric acid and a calcium-chloride column. The receiver and the trap were plunged in ice. The reaction flask was heated over an open flame with a Tecla burner. Decarboxylation began at 110°. As we determined in a preliminary experiment, the maximum evolution of carbon-dioxide gas occurs at a liquid temperature of 180°. The dibromofuran is not driven off, as the preliminary experiment indicated. Only after the water-jet pump is connected and the flow of illuminating gas is turned on does the distillation commence.

Later on, the pump and the flow of illuminating gas were started as soon as decarboxylation commenced. The temperature of the liquid was gradually raised from 180 to 220°. The reading of the upper thermometer (in the vapor) during this time was 120 to 121°. After distillation was complete, the product, which contained a large amount of quinoline, was poured into a separating funnel and washed twice with dilute acetic acid, and then with water, after which it was drained off in a flask containing an alkaline solution of hydroquinone (10% KOH, 5% hydroquinone). The yield of the crude product was 1.7 g (100% of the theoretical). Final purification was effected by distilling the product (3 g) in vacuum (12 mm) over calcined potash, with anhydrous nitrogen being passed through the liquid via a capillary tube. The product distilled at 46° (12 mm).

The boiling point determined in the capillary at 741 mm was 166.27° (corrected for the projecting length of column).

$$n_D^{25} \ 1.5458; \ d_{45}^{25} \ 1.99967.$$

2,3-Dibromofuran is a colorless substance with an odor that resembles iodoform somewhat. Upon standing in air it is rapidly resinified. As soon as it had been distilled, the product was poured into a previously weighed quantity of pure benzene, weighed, and filled into ampoules. The sealed ampoules

were stored in ice until the dipole moment was measured.

Carius Bromine Determination

For the bromine determination we took 0.2279 g of the benzene solution, containing 0.0716 g of the product. The results of analysis were as follows:

0.0716 g substance: 0.1193 g AgBr.

Found %: Br 70.95.

$C_4H_2Br_2O$. Calculated %: Br 70.77.

3. Measurement of the Dipole Moment of 2,3-Dibromofuran in Benzene at 25°.

The results of this measurement are listed in the table the second column containing the molar parts (f) of the dissolved substance times 100, the third column the solution densities (d), and the fourth column the solution dielectric constants (ϵ). The constants α and β and the total polarization of the substance at infinite dilution (P_∞) were computed by the Hedestrand method [3] from these data.

Solution No	$f \cdot 100$	d	ϵ
0	0	0.87247	2.2714
1	0.4264	0.87887	2.2866
2	0.6745	0.88263	2.2958
3	0.8421	0.88504	2.3019
4	0.9451	0.88665	2.3059
5	1.0933	0.88894	2.3112
Extrapolated	1.2000	0.89050	2.3148

$$\alpha = 3.6167; \beta = 1.5025; P_\infty = 84.40 \pm 0.52; R_D = 35.75.$$

SUMMARY

1. 2,3-Dibromofuran was synthesized and its constants determined: b.p. 166.27° (corr.) at 741 mm; d_{25}^{25} 1.99967; n_D^{25} 1.5458; dipole moment 1.53 D.

2. The structure of 2,3-bromofuran was established on the basis of its dipole moment and genetic bond, and the incorrectness of Hill's assertions concerning the structure of 3-bromo- and 3,5-dibromopyromucic acids was demonstrated. In fact, these are not 3-bromo- but 4-bromopyromucic, and not 3,5-dibromo- but 4,5-dibromopyromucic acids.

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SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

IV. SULFONATION OF INDOLE AND ITS HOMOLOGUES

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In the preceding report by A. Terentyev and L. Yanovskaya [1] it was shown that pyrrole and its homologues can be sulfonated with good yields by means of pyridine sulfotrioxide (the addition product of sulfur trioxide and pyridine). It was noted that at high temperature the reaction always occurs at the α -position of the pyrrole "finger" (to use N. Beketov's expression). When both alpha positions are occupied, the sulfo group does not enter into reaction even at 150°.

It was the objective of the present research to confirm the feasibility of sulfonating the indoles. In addition, it was important to establish the place where the sulfo group enters the indole system and to check the extent to which the relationship patterns observed in pyrrole and its homologues are borne out in this series of compounds.

In its behavior toward pyridine sulfotrioxide, indole greatly resembles pyrrole; we were able to sulfonate it without particular difficulty. In general, indole is not as acidophobic, i.e., sensitive to mineral acids, as pyrrole. It also proved to be somewhat harder to sulfonate. Thus, to obtain good yields with pyrrole, we had to effect the reaction in a solution of dichloroethane and keep the temperature from rising above 100°. We sulfonated indole without a solvent, and the best yields were obtained at 120°. At lower temperatures the reaction apparently stops at the stage of the N-sulfo-substitute. The latter underwent hydrolysis during further treatment of the sulfo mass by boiling with barium carbonate. We checked this behavior of indolesulfonic acid by synthesizing the acid through treating indole with pyridine sulfotrioxide in an alkaline solution. This was the method earlier employed by Baumgarten [2] and by Weidenhagen [3] for some amino derivatives. V. Ufimtsev [4] effected the N-sulfonation of hydrazobenzene by the same method.

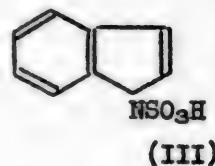
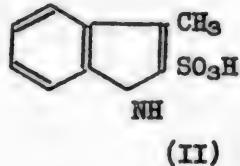
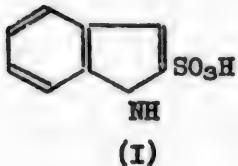
In fact, the barium salt of N-sulfoindole synthesized by us is cleaved fairly readily when boiled with alkaline solutions.

As for the place where the sulfo group enters the indole during sulfonation at high temperature, it was difficult to make any prediction with confidence. On the one hand, our experiments on the sulfonation of furan and pyrrole derivatives made us expect an alpha orientation. On the other hand,

a very large number of direct-substitution reactions occurs at the beta position in indole, as distinct from pyrrole.

The C-indolesulfonic acid synthesized by us proved to have a sulfo group at the alpha position of the pyrrole section of the indole system. We proved this by its direct conversion into the hydroxyindole by acid hydrolysis. It was also indirectly confirmed by the fact that pyridine sulfotrioxide proved to be able to sulfonate only β -methylindole, and not α -methylindole. This latter observation enabled us to make an even closer comparison of the behavior of indole and pyrrole. As was shown in the previous report by Terentyev and Yanovskaya, α, α' -dimethylpyrrole cannot be sulfonated.

As for the properties of the sulfo acids of the indole series, the introduction of the sulfo group stabilizes the indole, as might have been predicted. The salts of indole sulfonic acid are quite stable and dissolve readily in water, but are insoluble in organic solvents. Bromine water can split off the sulfo group fairly easily as sulfuric acid. In hydrolysis, the process continues, as we pointed out above, with evolution of sulfur dioxide as the sulfo group is replaced by hydroxyl. This was observed as early as 1888 by Hinsberg [5] in the naphthylindole sulfo acids, which he synthesized by a reaction of α - and β -naphthylamines with gloxalsodium bisulfite.



EXPERIMENTAL

Indolesulfonic-(2) acid (I). When indole is sulfonated with pyridine sulfotrioxide at a temperature of 80-100°, we get a yield that does not exceed 60% of theory. When the temperature was raised to 120°, we succeeded in obtaining higher yields. 2 g of indole and 5.6 g of pyridine sulfotrioxide were heated to 120° in a sealed tube for 10 hours. The reddish-brown sulfo mass was treated by boiling with an aqueous suspension of barium carbonate. The filtrate was decolorized by boiling with charcoal and then reduced to small volume, after which it was precipitated with alcohol. The yield was 4 g of the salt, i.e., about 90% of the theoretical yield, based on the monosulfo acid.

2.828 mg substance: 1.225 mg BaSO₄.

2.314 mg substance: 1.002 mg BaSO₄.

Found %: Ba 25.49, 25.48.

$(C_9H_6O_3NS)_2Ba$. Calculated %: Ba 25.93.

The barium salt is white, soluble in water, and slightly soluble in alcohol. Its reaction with bromine water results in the precipitation of bromine derivatives; after washing with alcohol and hydrochloric acid, barium sulfate is left.

Indolesulfonic-(2) acid (I) is obtained according to the following procedure: Indole (10 g) is dissolved in 10 ml of concentrated HCl. To this is added 10 ml of 50% conc. NaHSO₃ solution and the mixture is heated to 100°. After 10 minutes, the mixture is cooled to room temperature and the pH is adjusted to 7.0 with 10N NaOH. The product is collected, washed with water, dried, and recrystallized from 90% ethanol. Yield: 7.64 g. m.p. 206°-207°. Found: C 54.5, H 4.5, S 12.5%. Calculated: C 54.5, H 4.5, S 12.5%.

Boiling with 15% hydrochloric acid causes hydrolysis, with the evolution of sulfur dioxide. The acid solution was then extracted with ether. Evaporation of the solvent left behind a substance with a m.p. of 122°. The m.p. given in the literature for the expected hydroxyindole range from 120 to 126°. If the sulfo group were at the beta position, indoxyl should have been synthesized in this hydrolysis. But neither in the acid solution nor in melts with alkalies did we find even traces of indoxyl, which can be easily detected by converting it into indigo blue. The free sulfo acid was synthesized from the barium salt by treating the latter with sulfuric acid; it consists of easily deliquescing, hygroscopic, dark crystals with a m.p. of about 80°.

3-Methylindolesulfonic-(2) acid (II). A mixture of 2 g of skatole and 8 g of pyridine sulfotrioxide (molecular ratio = 1:3) was heated to 120° in a sealed tube for 10 hours. The dark-brown reaction mass was treated with barium carbonate as before. After the filtrate had been evaporated to small volume, the salt was precipitated by a mixture of alcohol and acetone.

This yielded 2.5 g of light-brown crystals. The yield was about 55%, based on the monosulfo acid.

3.713 mg substance: 1.565 mg BaSO₄.

Found %: Ba 24.80.

(C₉H₈O₃NS)₂Ba. Calculated %: Ba 24.65.

The salt is readily soluble in water, appreciably so in alcohol, and insoluble in organic solvents. It behaves like the respective α-indolesulfo acid when acted upon by bromine water or boiled with hydrochloric acid.

2-Methylindole (methylketole), which has no free alpha hydrogen, reacted otherwise than indole and skatole. We were unable to obtain a sulfo product by reacting it with pyridine sulfotrioxide at 120° and even at 170°. The extremely dark resinified reaction mass partially yielded the initial methylketole when treated with barium carbonate. Obviously, only an N-substitution product is formed in the reaction and is subsequently cleaved by boiling with barium carbonate.

Indolesulfonic-(1) acid. We were interested in synthesizing and examining the properties of the N-sulfo acid of indole, as this isomer is apparently the first product of the reaction when indole derivatives are sulfonated. 1 g of indole was suspended in 25 ml of water by heating and rapid cooling. After 8 g of baryta had been added, the mixture was precipitated with ice water, and 4 g of pyridine sulfotrioxide was added to it in small batches. The mixture was then agitated for 1.5 hours. The excess baryta was precipitated by a current of carbon-dioxide gas. After the precipitate of barium carbonate and sulfate and the indole that had not entered into the reaction had all been removed, the filtrate was evaporated with added ammonia. The barium salt of N-sulfoindole was separated from the water with alcohol. This yielded about 1 g of shining grayish brown crystals. The salt was purified by dissolving it in water and precipitating it with alcohol. It changes rapidly in the air, turning darker, which made its preparation in an analytically pure state difficult.

6.378 mg substance: 2.638 mg BaSO₄.

Found %: Ba 24.81.

(C₈H₆O₃NS)₂Ba. Calculated %: Ba 25.93.

When the barium salt is boiled with an aqueous solution of sodium hydroxide, it is hydrolyzed; the indole is driven off with steam, and barium sulfate precipitates out. We observed the same sort of phenomenon when treating the sulfo mass obtained by sulfonating indole at temperatures below 80°. Evidently, the sulfo group was first attached to the nitrogen atom, shifting to the alpha position when the temperature rose.

SUMMARY

Indole and skatole were sulfonated by heating to 120° with pyridine sulfotrioxide. Indolesulfonic-(2) acid and 3-methylindolesulfonic-(2) acid were synthesized as their barium salts and described. 2-Methylindole is not sulfonated even at 170°. A salt of indolesulfonic-(1) acid was synthesized by treating indole in an aqueous medium in the presence of baryta; it proved to be easily hydrolyzable in an alkaline solution.

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SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

V. SULFONATION OF VINYL ETHERS

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In previous reports by one of the present authors and his associates it was shown [1] that such sensitive compounds as furan, pyrrole, and indole, as well as their derivatives, can be sulfonated with good yields by heating them with pyridine sulfotrioxide. In every case the alpha hydrogen atom was replaced by a sulfo group. Thus, notwithstanding the marked unsaturated nature of such compounds as furan and sylvan, for example, a substitution reaction takes place rather than an addition reaction.

In its structure furan may be compared to the ethers of vinyl alcohol. It thus was of some interest to investigate the behavior of vinyl ethers with the same reagent - pyridine sulfotrioxide. The ethers of vinyl alcohol polymerize very easily; they are resinified at once by the action of strong sulfuric acid. Pyridine sulfotrioxide likewise causes considerable resinification when acting directly. But when various precautions are taken, the reaction can be carried out normally, although with fairly low yields.

EXPERIMENTAL

We did our research with n-butyl vinyl ether, which was available to us. It was carefully purified and distilled twice over metallic sodium; b.p. 93-94°. 6.4 g of pyridine sulfotrioxide was added a bit at a time to an ice-chilled solution of 2 g of the butyl vinyl ether in 25 ml of dichloroethane. The mixture turned dark. The reaction progressed very slowly however in the cold and even at room temperature. It was then heated in a sealed tube for 6 to 8 hours at 60-70°. The dark sulfo mass was converted into the barium salt by boiling it with an aqueous suspension of barium carbonate until all the pyridine had been removed. The filtrate was evaporated to slight volume and precipitated with alcohol. The yield was 3.5 g of the barium salt. Analysis indicated that two molecules of sulfur trioxide enter into reaction with each molecule of the vinyl ether.

7.030 mg substance: 3.810 mg BaSO₄.

4.700 mg substance: 2.570 mg BaSO₄.

Found %: Ba 31.89, 32.17.

C₈H₁₂O₈S₂Ba·H₂O. Calculated %: Ba 31.84.

We were unable to eliminate the water by boiling, as this causes the salt to blacken and partially decompose.

Isoamyl vinyl ether was subjected to the same treatment with pyridine sulfotrioxide. The barium salt synthesized was quite similar to that of the butyl vinyl ether.

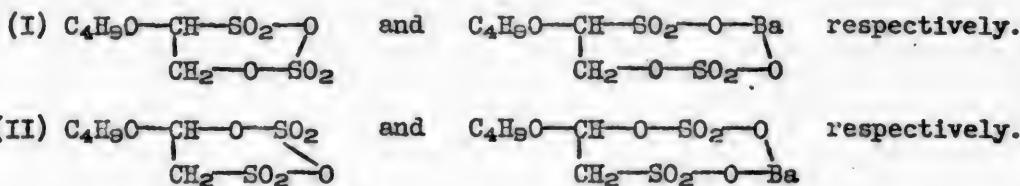
7.950 mg substance: 4.160 mg BaSO₄.

4.750 mg substance: 2.510 mg BaSO₄.

Found %: Ba 30.80, 31.09.

C₇H₁₄O₈S₂Ba·H₂O. Calculated %: Ba 30.82.

The barium salt synthesized in the reaction with the butyl vinyl ether does not bleach bromine water; it forms barium sulfate rather easily when boiled with acids. All this indicates that two molecules of sulfur trioxide are added to the double bond of the ether when it is reacted with pyridine sulfotrioxide. Thus, the synthesized product has a structure of the carbyl sulfate type. When treated with baryta it yields a derivative of ethionic acid. Two formulas may be written for the product synthesized:



From the theoretical standpoint, the more likely of these is the first one. Investigation of its hydrolytic cleavage likewise confirms this conjecture. Acid hydrolysis of the first compound ought to result in some splitting off of sulfurous acid in addition to the sulfuric acid formed, since an aldehyde bisulfite is formed after the butyl alcohol is eliminated. The compound corresponding to the second formula ought to split off butyl alcohol and sulfuric acid readily during hydrolysis, being converted into sulfoacetic aldehyde. When it was boiled with 25% hydrochloric acid, barium sulfate was quickly precipitated, and butyl alcohol was distilled with steam. No sulfurous acid was formed, only negligible cloudiness (due to barium chloride) being observed in the distillate's aqueous layer after treatment with bromine water. To study the reaction products more closely, the barium salt was boiled with 30% sulfuric acid for 20 minutes. Butyl alcohol was driven off. The reaction mass was treated with an excess of barium carbonate. The filtrate was evaporated to slight volume; a white salt was precipitated from it by adding alcohol. The salt was analyzed after repeated recrystallization from water.

3.230 mg substance: 2.022 mg BaSO₄.

3.367 mg substance: 1.997 mg BaSO₄.

Found %: Ba 34.68, 34.83.

(C₂H₃O₄S₂)Ba·H₂O. Calculated %: Ba 34.22.

Analysis and properties indicate that this salt corresponds to the barium salt of sulfoacetic aldehyde.

Sulfoacetic aldehyde was synthesized by Schroeter in 1919 [2] from methanedisulfonic acid by a rather complicated method. Its barium salt, which was readily soluble in water, crystallized with one molecule of water; this was also observed to be the case in our experiment.

The barium ethanalsulfonate synthesized by us exhibited the characteristic color with Schiff's reagent and reduced a solution of ammoniacal silver nitrate.

Thus, the reaction studied by us opens the way to the synthesis of sulfoacetic aldehyde and its analogues.

The reaction of pyridine sulfotrioxide with the vinyl ethers studies by us is quite similar to the reaction of these ethers with mercury salts recently described by A. Nesmeyanov, I. Lutsenko, and N. Vereshchagina [3]. Hydrolysis of the product of the addition of mercury acetate to vinyl ethers yields mercurated acetaldehyde, with good yields.

SUMMARY

The action of pyridine sulfotrioxide on the ethers of vinyl alcohol results in the addition of two molecules of sulfotrioxide at the double bond. Sulfoacetic aldehyde is formed in the acid hydrolysis of the barium salt of the acid synthesized.

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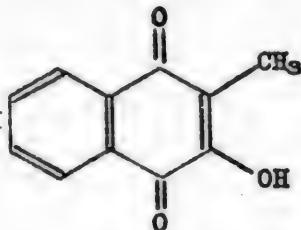
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THE CHARACTERISTICS OF PHTHIOCOL

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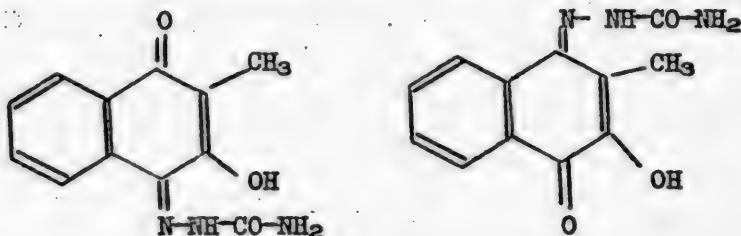
Phthiocol was first discovered by Anderson among natural objects during his investigation of the saponification products of the neutral fat of the human bacillus tuberculosis [1]. Anderson states that this yellow pigment is a metabolism product of Mycobacterium tuberculosis var. hominis and is contained in them in both the free and the latent states [2]. But not all authors agree with Anderson in this. Thus, A N Parshin [3] believes that the phthiocol isolated from the human tuberculosis bacillus by Anderson's method [4] is a secondary product formed as the result of the saponification of some more complex compound? Besides, according to the data published by D.W. Wooley and Janet R. McCarter [5], phthiocol is a growth factor for Mycobacterium phlei. But, no matter what its origin, phthiocol is of interest because of the fact that, possessing the structure of 2-methyl-3-hydroxy-1,4-naphthoquinone (I), its chemical composition is close to that of the compounds of the Vitamin K₁ and B₂ group:



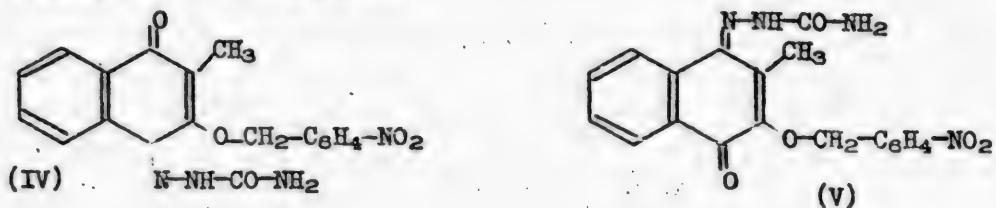
From the biological standpoint, phthiocol was also found to be very close to this group of compounds. Thus, H. J. Almquist and A.A. Klose [6] came to the conclusion that, although the action of phthiocol is much weaker than that of Vitamin K₁, it still should be included among the compounds possessing antihemorrhagic activity. Other authors [7] also mention phthiocol's antihemorrhagic action.

The chemical closeness of phthiocol to the compounds of the Vitamin K₁ group, as well as its antihemorrhagic properties, which enabled it to be employed as a blood-stopping remedy in clinics [8], increased interest in this compound. Moreover, in recent years phthiocol has been employed as the initial compound in several investigations of the mechanism of the oxidative hydrolytic cleavage of quinones undertaken by M.M. Shemyakin, L. A. Shchukina, Y.B. Shvetsov,

and E.I. Vinogradova [8]. The chemical description of this compound is very poorly covered in the literature, however. Phthiocol is most simply synthesized from 2-methyl-1,4-naphthoquinone oxide [10]. Of its derivatives, only phthiocol acetate, its monooxime, and a few esters are known [11]. That is why it seemed to be rather desirable to study in detail the behavior of phthiocol with various reagents in order to expand its characterization. It was ascertained that at room temperature phthiocol does not react with semicarbazide. But phthiocol semicarbazone can be synthesized, however, by carrying out the reaction by heating it for 8 hours in an aqueous alcohol solution. Under these reaction conditions, the semicarbazone is obtained in a highly contaminated state, mixed with unreacted phthiocol and with other impurities whose properties are close to those of the phthiocol semicarbazone. Because of this, very careful refining was required; this refining should be done by washing the semicarbazone with water and then with alcohol, after which it is subjected to prolonged extraction with hot ether until all the phthiocol has been eliminated and then crystallized from ethyl or propyl alcohol. Judging by the elementary analysis, the semicarbazone synthesized is a phthiocol monosemicarbazone. It may have the structure represented by either formula (II) or formula (III). By analogy with other 2-methyl-substituted naphthaquinones, it probably possesses structure (II):



It should be noted that the synthesis of phthiocol semicarbazone in an analytically pure state requires that it be converted into the mono-sodium salt by the action of a hot 5% solution of sodium hydroxide; this salt can be readily crystallized from a minimum quantity of water. The monosodium salt crystallizes as beautiful, silky, orange-yellow needles and contains one molecule of water of crystallization. The latter may be eliminated by heating the salt to 140° in a 7-mm vacuum for a long time, but when exposed to the air it quickly absorbs water again. The action of 10% sulfuric acid upon the mono-sodium salt refined by recrystallization from water yields the initial phthiocol semicarbazone, which is a crystalline substance with a decomposition temperature of $234\text{--}235^\circ$ after recrystallization from propyl alcohol. Moreover, the p-nitrobenzyl ether of phthiocol semicarbazone, with a m.p. of 205° , can be readily synthesized from the monosodium salt. Its structure may be either that of formula (IV) or formula (V):



EXPERIMENTAL

1. Synthesis of phthiocol semicarbazone and of its sodium salt. A solution of 1.14 g of trihydrated sodium acetate and 1.14 g of semicarbazide hydrochloride in 30 ml of water is added to 2 g of phthiocol, dissolved in 60 ml of hot ethyl alcohol. When the reagents are mixed together, the solution turns raspberry-red. The reaction mass is then heated over a water bath for 8 hours. After cooling, 1.1 g of an orange-yellow precipitate, phthiocol semicarbazone, settles out. When the mother liquor is diluted with water, another 1 g of the substance is precipitated. The two precipitates are combined, carefully washed, first with water and then with alcohol, dried in the air, carefully comminuted, and extracted with hot ether until there is absolutely no more phthiocol left in the precipitate (the wash water does not turn red with a solution of sodium hydroxide). Then the substance is dissolved in 450 ml of hot ethyl alcohol and filtered, and the solution obtained is evaporated to a volume of 200 to 250 ml. The precipitate that settles upon cooling is filtered out and dissolved in a minimum quantity of a hot solution of 5% sodium hydroxide. Upon cooling, the beautiful, silky, orange-yellow needles of the sodium salt of phthiocol semicarbazone settle out; they are filtered out, recrystallized three times in the presence of activated charcoal from a minimum quantity of hot water, and dried in a 10-mm vacuum at 105-110°. The sodium salt crystallizes with 1 molecule of water of crystallization, which it is impracticable to remove under these drying conditions.

Found %: C 50.36; H 4.23; N 14.69; Na 7.66.
 $C_{12}H_{10}O_3N_3Na \cdot H_2O$. Calculated %: C 50.52; H 4.21; N 14.74; Na 8.07.

The synthesized sodium salt of phthiocol semicarbazone is dissolved in cold water, and a 10% solution of sulfuric acid is added until an acid reaction is obtained with Congo red. This causes a light-yellow precipitate of phthiocol semicarbazone to settle out. The precipitate is filtered out, washed with water to remove the acid, dried in the air, recrystallized from propyl alcohol and then dried in vacuum at 7-9 mm and 120-130°. The decomposition temperature of phthiocol semicarbazone is 234-235°.

Found %: C 58.69; H 4.32; N 17.35.
 $C_{12}H_{11}O_3N_3$. Calculated %: C 58.77; H 4.08; N 17.14.

2. Synthesis of the p-nitrobenzyl ether of phthiocol semicarbazone. A solution of 0.38 g of p-nitrobenzyl bromide in 4 ml of hot alcohol is added to a solution of 0.5 g of the sodium salt of phthiocol semicarbazone in 2 ml of water. The solution is heated over a water bath. After a few minutes have passed, a yellow precipitate begins to settle out. Heating is continued for an hour. Then the reaction mass is cooled, and the precipitate filtered out and washed with water. Weight: 0.7 g. The precipitate is dissolved in 130 ml of hot ethyl alcohol and set aside to stand in the cold at a temperature of -5°. The next day the precipitate, the p-nitrobenzyl ether of phthiocol semicarbazone is filtered out. Weight of the precipitate 0.4 g; m.p. 205°.

Found %: C 60.21; H 4.35; N 14.87.
 $C_{19}H_{18}N_4O_5$. Calculated %: C 60.00; H 4.21; N 14.74.

SUMMARY

The synthesis of some derivatives of phthiocol is described: phthiocol semicarbazone and its monosodium salt, as well as the p-nitrobenzyl ether of phthiocol semicarbazone.

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TABLE OF CONTENTS (Continued)

	page	Russ page
103. Derivatives of Zingarone. <u>Berlin, Sherlin, and Serebrennikova</u>	739	759
104. The Formation of Oxazolones from Acyl Derivatives of Glycine. <u>Shemyakin, Lurye, Rodionovskaya</u>	749	769
105. The Synthesis of 4-Chloro- and 4-Bromo-1-Aminanthraquinone and of Their Benzoyl Derivatives by the Sandmeyer Reaction. <u>Mozgova</u>	755	773
106. Synthesis of 2,3-Dibromofuran and the Structure of 3-Bromo and 3,5-Dibromopyruvic Acids <u>Nazarova and Syrkin</u>	759	777
107. Sulfonation and Sulfo Acids of Acidophobic Compounds. IV. Sulfonation of Indole and Its Homologs. <u>Tarantyev, Golybaya, and Taybal</u>	763	781
108. Sulfonation and Sulfo Acids of Acidophobic Compounds. V. Sulfonation of Vinyl Ethers. <u>Tarantyev and Volynsky</u>	767	784
109. The Characteristics of Phthiocol. <u>Vinogradova</u>	771	787



